# REPORT OF THE CHIEF OF THE BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, 1946

UNITED STATES DEPARTMENT OF AGRICULTURE,
*Washington, D. C., September 3, 1946.*

Mr. P. V. CARDON,
*Agricultural Research Administrator.*

DEAR MR. CARDON: I present herewith the report of the Bureau of Agricultural and Industrial Chemistry for the fiscal year ended June 30, 1946.

Sincerely,

LOUIS B. HOWARD, *Chief.*

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## INTRODUCTION

During the past fiscal year certain projects of the Bureau of Agricultural and Industrial Chemistry that had been started or expanded in order to contribute to the Nation's war effort were discontinued, curtailed, or redirected toward peacetime objectives, and other projects that had been suspended or relatively inactive during the war were given more attention. Some of the larger or more important wartime projects of the Bureau were those dealing with: The selection of micro-organisms, culture media, and conditions to increase the yield of penicillin; the fermentative production of butylene glycol and its conversion to butadiene for possible use in the manufacture of synthetic rubber; the extraction of natural rubber from plants grown in the United States; the dehydration and compression of vegetables and eggs; the design of a large-capacity machine to cut lint cotton to short lengths so it could be nitrated like cotton linters; more rapid stabilization of nitrated cotton for use in explosives; improving the properties of cotton tire cord; and improving the serviceability of military fabrics made of cotton. Some of the projects mentioned have been closed, and others continued for their potential peacetime contribution.

Although surplus problems have not yet reappeared, except in the case of potatoes, there is need for continued work in that field so that we will be in a better position to cope with the situation should they again occur.

Attention is being directed especially toward the development of nonfood uses for edible farm commodities and to the expansion of uses for inedible agricultural products and byproducts.

This report gives examples of the various kinds of research activity that were in progress during the fiscal year 1946, with brief statements on the more important accomplishments and their significance. More complete and detailed information on various activities and their results is given in the 294 publications issued during the year. Most of these were original reports of research which appeared in scientific

and trade journals. Information on newly developed processes and products is also given in the specifications of the 29 public service patents granted during the year to employees of the Bureau. A list of publications issued and patents granted during the fiscal year 1946 is available in mimeographed form.

Most of the members of the scientific, clerical, and maintenance staffs of the Bureau who were in the armed services of the United States during the late war have returned to their jobs. Several experts in chemistry and chemical engineering were loaned temporarily to the Technical Industrial Intelligence Committee of the Foreign Economic Administration to investigate the status, equipment, and processes of certain industries in Germany and other countries occupied by the United Nations. These experts made detailed reports of their observations, some of which have been released for publication to aid American industries and agriculture.

The Guayule Rubber Extraction Unit, which had conducted laboratory and pilot-plant experiments at Salinas, Calif., as part of the Department's emergency rubber investigations, was closed during the year. In the Western Regional Research Laboratory, the Commodity Processing Division, the Commodity Byproducts Division, and the Protein Division were abolished and their staffs were divided between the Food Products Division and the Industrial Products Division which were newly established. In the Northern Regional Research Laboratory, the Agricultural Motor Fuels Division was abolished and its personnel divided between three already existing divisions.

The administrative officers of the Bureau and heads of its research laboratories and divisions, as of June 30, 1946, are listed below.

BUREAU ORGANIZATION AT END OF FISCAL YEAR 1946

| | |
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| Chief of Bureau | Louis B. Howard. |
| Assistant Chief | Carl F. Speh. |
| Assistant Chief | Henry A. Donovan. |
| Agricultural Chemical Research Division. | Lawrence F. Martin, Head. |
| Allergens Research Division | Henry Stevens, Head. |
| Biologically Active Compounds Division. | George W. Irving, Jr., Head. |
| Enzyme and Phytochemical Research Division. | Arnold K. Balls, Head. |
| Fruit and Vegetable Chemistry Laboratory. | Elmer A. Beavans, in charge. |
| Fruit and Vegetable Products Laboratory. | Alfred M. Neubert, in charge. |
| Microbiology Research Division | Vernon H. McFarlane, Acting Head. |
| Naval Stores Research Division | Ismond E. Knapp, Head. |
| Pharmacology Laboratory | Floyd De Eds, Head. |
| Synthetic Liquid Fuels Project | John W. Dunning, in charge. |

NORTHERN REGIONAL RESEARCH LABORATORY, PEORIA, ILL.

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| Agricultural Residues Division | Elbert C. Lathrop, Head. |
| Analytical and Physical Chemical Division. | Reid T. Milner, Head. |
| Commodity Development Division | Joseph H. Shollenberger, Head. |
| Engineering and Development Division | Cecil T. Langford, Head. |
| Fermentation Division | Asger F. Langlykke, Head. |
| Oil and Protein Division | John C. Cowan, Head. |
| Starch and Dextrose Division | Carl E. Rist, Acting Head. |

SOUTHERN REGIONAL RESEARCH LABORATORY, NEW ORLEANS, LA.

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| Director | Walter M. Scott. |
| Assistant Director | Harry P. Newton. |
| Analytical, Physical Chemical, and Physical Division. | Turner H. Hopper, Head. |
| Cotton Chemical Finishing Division | James D. Dean, Head. |
| Cotton Fiber Research Division | W. Kyle Ward, Jr., Head. |
| Cotton Processing Division | Robert J. Cheatham, Head. |
| Engineering and Development Division | Edward A. Gastrock, Head. |
| Oil, Fat and Protein Division | Klare S. Markley, Head. |
| Sweetpotato Products Division | Paul R. Dawson, Head. |

EASTERN REGIONAL RESEARCH LABORATORY, WYNDMOOR, PA.

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| Director | Percy A. Wells. |
| Assistant Director | Rex E. Lothrop. |
| Analytical and Physical Chemistry Division. | Michael J. Copley, Head. |
| Biochemical Division | John J. Willaman, Head. |
| Carbohydrate Division | Lee T. Smith, Head. |
| Chemical Engineering and Development Division. | Roderick K. Eskew, Head. |
| Hides, Tanning Materials, and Leather Division. | Jerome S. Rogers, Head. |
| Oil and Fat Division | Waldo C. Ault, Head. |
| Protein Division | Richard W. Jackson, Head. |

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| Director | Theodore L. Swenson. |
| Biochemical Division | Howard D. Lightbody, Head. |
| Engineering and Development Division | Wallace B. Van Arsdel, Head. |
| Food Products Division | John R. Matchett, Head. |
| Industrial Products Division | George H. Brother, Head. |
| Physicochemical and Analytical Division. | Charles H. Kunsman, Head. |

## USEFULNESS OF COTTON FABRICS EXTENDED BY CHEMICAL FINISHING

If cotton is to maintain or expand its markets, it must be able to meet consumer requirements better than competing fibers. Existing cotton products must be improved and new cotton products developed.

For several years the bulk of the domestic cotton crop has consisted of short-staple cotton, of which a considerable portion has gone into industrial fabrics receiving little, if any, chemical finishing treatment. Research to improve appearance and broaden utility of this low-grade product was undertaken at the Southern Regional Laboratory. Such fabrics as part-waste osnaburg and bag sheetings have been finished on a semicommercial scale by standard methods that include kier boiling, bleaching, mercerizing, and dyeing with fast vat colors. These finished fabrics, originally limited to bagging and similar low-cost products, may now be used for garments, draperies, slip covers, and similar materials. By the proper employment of regular commercial finishing processes these goods can be converted at a reasonable cost into attractive fabrics suitable for numerous other uses. As with higher-quality cotton materials, the properties of this low-grade product are improved by applying a treatment to prevent shrinkage during laundering.

The report for 1945 mentioned the excellent rot resistance of partially acetylated cotton fabrics. The publication of results with this rotproofing treatment in trade and technical journals has resulted in numerous inquiries about the process and the product; also in requests for samples and for processing of the inquirers' own goods. Several new uses have been suggested including boat lining, seedbed covers, cloth bags for use in water-softening systems, bags for covering hams for overseas shipment, yarn for electrical insulation in tropical climates and fish-net twines. As a consequence of the great interest shown, small lots of partially acetylated yarns, threads, and fabrics have been sent out to different organizations for tests for various uses and larger lots of cloth have been prepared for service tests in water-softening bags and for seedbed covers. During the past year research has been on a pilot-plant scale to obtain materials for testing and to determine whether existing commercial finishing machinery could be adapted to the partial acetylation process. New-type equipment is probably not required, since medium-weight full-width piece goods in lengths up to 75 yards were successfully processed on a dye jig.

An extensive service trial of cotton sandbags rotproofed with copper compounds, covering a period of 19 months, was completed on October 1, 1945. The test, in which 165 standard-sized bags were used, supplied practical information about the relative effectiveness of various proofing agents in protecting cotton fabrics against biological rotting, when exposed under severely degrading natural conditions, and confirmed satisfactorily the dependability of accelerated soil burial as a method of gaging the effectiveness of rotproofing treatments. A final report on the test was made to the War Department, and an article summarizing its more important features was accepted for publication in American Dyestuff Reporter for July 15, 1946.

In order to develop better protective treatments against the damaging effects of weather exposure, it is desirable to understand as fully as possible the mechanism of cellulose break-down when cotton fabrics are exposed to sunlight as well as the manner in which this process is influenced by the presence of various chemicals or finishes which the fabric may have received. To this end, both plain and chemically finished fabrics have been exposed to weather with the latter group including representative pigment and other protective treatments. By means of systematic examination of the degradation occurring in the various samples, an attempt is being made to isolate, so far as possible, individual factors in the composite of destructive forces found in weathering, and to evaluate each of these in respect to its effect upon cotton cellulose. For this purpose a new type of exposure cabinet, which moves so that flat samples of fabrics continuously face the sun throughout the day, was designed and built. In this cabinet the fabric samples are mounted behind color filters, each of which transmits a different fraction of the sun's light. The samples are maintained at constant temperature and moisture content in an atmosphere of purified air, and periodically small portions are removed and examined. Exposure data obtained on both the experimental and the commercially finished fabrics will be useful as a guide to industry, as well as to future research at the Southern Regional Laboratory.

Among the various treatments examined, those that deposit mineral pigments on the fiber, such as lead chromate and iron tannate, have appeared to be the most effective in resisting the destructive action of sunlight and other weathering factors on cotton cellulose. Since the color imparted to fabrics by application of mineral pigments tends to limit their range of usefulness, attention has also been given to the possibility of utilizing, for protection against sunlight, other materials that do not noticeably color the treated fabric. For example, a form of urea-formaldehyde resin that is light in color has been observed to retard the degradation of cotton exposed to carbon-arc radiations, and cloth treated with this compound is being tested for resistance to deterioration by sunlight.

### WIND- AND RAIN-RESISTANT FABRIC BEING DEVELOPED

During the past year, the development of an improved, wind- and rain-resistant, Oxford-type cotton fabric for civilian and army use was undertaken in cooperation with the Office of the Quartermaster General. Experimental work in this broad project included: Determination of fundamental relationships of moisture to cotton cellulose; measurement of changes in physical dimensions of fibers and yarns upon wetting; evaluation of the effect of variety of cotton; design of yarn and fabric construction; and development of finishing treatment.

From tests on experimental fabrics manufactured at the Southern Regional Laboratory, it was found that improved water resistance can be obtained in Oxford-type cotton fabric by employing one or more of the following means: Use of mercerized yarn; addition of a swellable coating material (such as hydroxyethylcellulose) to the yarn before weaving; insertion of extra filling picks by means of a special loom attachment; and the selection of a variety of cotton whose fibers swell more in contact with water than do those of common varieties, thereby producing a yarn and fabric more resistant to the passage of water. To promote effective prosecution of the project, a bibliography was prepared. It consists of about 750 abstracts covering the literature for the past 20 years on the swelling of cotton and related subjects, and particularly articles that deal with the relationship between cotton cellulose and water. Through the cooperation of the Department of Agriculture Library, copies of this bibliography were to be available by the end of 1946.

### COMMERCIAL COTTON BLEACHERIES SURVEYED

Commercial cotton bleacheries employ a number of processes, partly from tradition and partly due to the great variety of cotton goods treated. In order to evaluate average practice and to establish a basis for judging future developments, a survey was made of 12 bleaching processes at 4 plants. Materials and conditions of operation were observed; samples of cloth were taken at the most important stages of processing; and physical-chemical tests were made on the samples at the Southern Regional Laboratory. Industry has welcomed the first part of the detailed report which appeared in American Dyestuff Reporter for June 3, 1946. The main part of the survey will be reported in a technical bulletin which is being prepared for publication.

## TIRES CONTAINING CORDS OF SELECTED COTTON GIVE GREATER SERVICE

The Southern Regional Laboratory has continued its broad coordinated program of research on the improvement of cotton tire cord in an effort to help cotton meet the ever increasing competition from rayon. Since the end of the war the objectives have been redirected, and primary consideration is now being given to the service requirements of cord in tires for civilian use.

In November 1945, release was obtained from the War Department of data acquired during the war on Army service tests of Southern Regional Research Laboratory experimental tires, and summaries were prepared and published in newspapers and trade journals. These tires, which were 7.50–20, S4 military truck tires, were made from 3 selected varieties of cotton (Stoneville 2B, Wilds 13, and SXP) with tires made from regular commercial cotton cord as controls. In these tests, with the commercial cotton cord tires rated at 100, the Stoneville 2B cord tires gave a performance of 138, the SXP tires 200, and the Wilds 13 cord tires a performance of 253. Data were also released by the War Production Board on service tests run on light truck tires made from Wilds cotton cord, rayon cord, and regular commercial cotton cord. These tires were 7.00–20, S4 type with highway treads. The Wilds cotton-cord tires gave an average mileage of three times that obtained with the commercial cotton-cord controls. The rayon-cord tires gave a slightly higher mileage than the Wilds cotton-cord tires, but the difference was not considered significant in determining the relative value of cotton and rayon for this size of tire.

Service and indoor wheel tests are now under way on 9.00–20, S6, 10-ply cotton tire cords made with (1) a commercial company's regular production cotton cord, (2) Wilds cotton cord produced according to company's regular process, and (3) Wilds cotton cord produced according to the dual-stretching process developed at the Southern Regional Laboratory. A similar set of rayon-cord tires is being run along with the cotton-cord tires to obtain comparative data on growth, tread wear, and operating temperatures. The wheel tests are being run by the National Bureau of Standards; the service tests are on trucks operating out of New Orleans, and representing a wide range of loads, speeds, and tread-wear conditions.

A ply-building machine was constructed for preparing tire plies for use in connection with the manufacture of tires for wheel and small-scale road tests. With this machine, the plies can be made from a single end of cord, the quantity required being only slightly in excess of the actual poundage of fabric in the finished tire. The plies so made are cut to the proper bias angle and shipped to a tire plant where they are made up into bands and thence directly into tires, bypassing the dipping and calendering operations completely. Previously, it was necessary to make up several hundred pounds of cord and to supply tire companies with several hundred yards of fabric, even when only a few tires were to be made. The use of the ply-building machine will greatly facilitate the wheel and service testing part of the tire-cord research program.

In a general survey of the effect of moisture and temperature on certain elastic properties of tire cords, it was found that, in general,

moisture content, over the ordinary range, has much greater effect on such properties than does temperature up to 145° C.

Continued research on the influence of cord construction on tire-cord properties showed that the amount of twist in the single yarns is a relatively unimportant factor, as regards strength and durability under flexing, but that a slightly higher twist in the plies than is customary in commercial practice gives greater durability under flexing. The strengths of five different constructions (5- and 4-ply in two-cable and 5-, 4-, and 3-ply in three-cable) are practically the same for each gage, but the durability under flexing, as measured on two types of flex-fatigue instruments, was decidedly greater for the three-cable construction.

Preliminary research on the chemical degradation of the cellulose of cotton tire cord, as indicated by cuprammonium fluidity measurements, showed that greater degradation occurred in the wheel-tested tires than in the road-tested tires, and there was an indication that some degradation occurred during the manufacturing process. Additional research on the influence of heat on the chemical degradation of cellulose is in progress.

## DISK-TYPE COTTON CUTTER OPERATED IN PRODUCTION TESTS

In the report for 1945, it was stated that the chemical-cotton supply was assured by the development of a new machine for rapidly reducing lint cotton to short-length fibers resembling linters. That report, made while this Nation was still at war, emphasized the need for an adequate supply of chemical-cotton for nitrocellulose and other products for war uses. Because of the relation of this machine to national defense, construction was completed and production tests were made. These proved that the two disk-type, cotton-cutter units, and auxiliary equipment will cut lint cotton so it can be converted into chemical cellulose by linters-purification plants. In the tests, made under the supervision of Southern Regional Laboratory engineers, 86 bales of low-grade sample cotton were cut, and two complete digester charges of nearly 7,000 pounds each were made without interruption. The rate of cutting was 111 pounds per minute, which is less than one-third of the rated capacity. Part of the difficulty was due to the many sample tags which materially reduced the intake of lint by the saw teeth of the feeder. With regular cotton and after certain practicable changes, the expected capacity of 350 pounds per minute should be attained. No further work on this project is contemplated.

## ADDITIONAL COTTONSEED PIGMENTS DISCOVERED

Scientists at the Southern Regional Research Laboratory are rapidly accumulating new knowledge on the chemistry of cottonseed pigments. Eleven colored compounds, in addition to the long recognized gossypol, have been detected. Based on the observation that most pigments are found in distinct glands, a process has been devised which separates cottonseed meats into three fractions: Oil, pigment glands, and gland-free meal. About 1,200 pounds of cottonseed flakes have been processed, from which 21 pounds of pigment glands and 200 pounds of gland-free meal have been obtained. This is the first time that these materials have been collected in such large quantities.

For years, persons familiar with cottonseed or the cottonseed processing industry have observed the blue-black coloration of the kernel and the red to black color of the expressed oil. Despite the innumerable observations of this dark pigmentation, only one pigment, namely light-yellow gossypol, had been isolated from cottonseed until recently. To this pigment has been attributed a multitude of problems associated with cottonseed and its products.

The Southern Regional Laboratory began work on the pigments of cottonseed about 4 years ago. Of the 11 pigments that have been recently detected, 3 have been isolated. Because of their colors and occurrence in cottonseed, these have been named gossypurpurin (purple-colored), gossyfulvin (orange-colored), and gossycaerulin (blue-colored). The last-mentioned pigment has been found only in cooked cottonseed meats. Most of these compounds have been found to reside in special organs of the seed which are generally referred to as pigment glands. These glands, the blue-black dots visible in a section of cottonseed, were observed to be walled-off bodies, apparently unconnected with the surrounding tissue. On the basis of the observation that their density is less than that of any other fraction of cottonseed, as well as the fact that the gland walls are not affected by certain solvents, a new type of process was developed, whereby cottonseed meats can be separated into three fractions.

In this process the meats are rolled into thin flakes and disintegrated by violent agitation in a liquid medium which effects a separation by flotation into intact pigment glands, an oil-solvent mixture, and a meal free of pigment glands and low in oil. The liquid medium in which this disintegration and separation are accomplished is a mixture of chlorinated and unchlorinated solvents adjusted to a density that allows the pigment glands to float to the surface and the particles of meal to sink to the bottom, leaving the oil-solvent mixture as an intermediate layer. Since practically all of the pigments of the gossypol group are removed in the form of intact glands, the meal and oil are relatively light-colored. The protein content of the meal is increased both by the removal of the glands, which amount to about 3 percent of the weight of the meal, and by the nearly complete removal of the oil.

The process in its present stage of development is not suitable for commercial use, although it is being operated in small-scale equipment. Further development research will be conducted on a pilot-plant scale in an effort to make the process commercially feasible for making light-colored cottonseed oil and meal.

Despite many years of research by various groups on the chemical, physical, nutritional, and toxicological properties of cottonseed, its products and constituents, there are many conflicting reports in the technical and trade literature which have not been fully explained. With the relatively pure materials made available by the Southern Regional Laboratory's new process, an investigation has been started by the Bureau's Pharmacology Laboratory to determine chronic toxicities of the pigment glands of cottonseed. It is to be expected that this fundamental investigation will provide basic information useful in promoting more extensive utilization of cottonseed.

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## SARELON, A NEW FIBER, MADE FROM PEANUT PROTEIN

Sarelon is the name given to a new artificial fiber made from peanut protein. As far as known, the Southern Regional Laboratory was the first laboratory in the United States to produce fibers from peanuts. Sarelon has a light cream color and a soft, pleasant feel intermediate between the natural protein fibers silk and wool. In heat-insulating and moisture-absorbing properties, Sarelon resembles wool. It does not shrink appreciably in hot water. It has an affinity for the dyes used on silk and wool. Solid shades can be obtained by dyeing mixed wool and Sarelon yarns with level-dyeing acid dyestuff from a boiling dye bath containing Glauber's salt and acid. Sarelon can also be successfully dyed with vat and direct cotton dyestuffs, which makes possible, by proper selection, the solid-shade dyeing of a mixed cotton and Sarelon yarn. The major weakness of Sarelon, as in other synthetic protein fibers, is its low wet strength. The treatments employed in the production of casein fiber to increase wet strength generally have but little effect on peanut-protein fibers. Although further efforts will be made to improve this property, significant development may have to await a better understanding of the structure of the peanut-protein molecule and means for its modification.

The raw material for the production of Sarelon is protein from solvent-extracted peanut meal. Peanut kernels have thin skins, usually of a reddish-brown color, and if the skins are not removed or destroyed, their pigments impart objectionable color to the meal and protein preparations. Light-colored protein is essential, and lack of a means for obtaining such protein has been a stumbling block in utilization of peanut meal for fibers, adhesives, and paper coatings. Removal of the skins by the blanching process, generally employed in the food industries, is not considered feasible in processing peanuts for oil and meal since it is costly and ordinarily subjects the kernels to a temperature high enough to partly alter the protein. White-skinned peanuts, successfully used in early work on Sarelon, are grown on a very limited scale. The color problem, however, is now believed to be solved by the development of a simple and inexpensive process in which kernels of common commercial varieties are dipped in a dilute lye solution, rinsed, and dried at room temperatures prior to the removal of the oil. A public-service patent to cover this process has been applied for.

Sarelon is made by a "wet" process similar to that employed in the viscose-rayon industry. The actual spinning operation, however, is much more complicated in the production of Sarelon than in the production of normal-strength, viscose-rayon yarns. The spinning solution usually contains 18–24 percent peanut protein and is made by dissolving the peanut protein in dilute lye, adding, as desired, such modifiers as oils, emulsifiers, or plasticizers, aging the solution for 2 hours, and centrifuging to remove entrapped air. Extrusion of this solution through small holes into a coagulating bath, containing 5 percent of sulfuric acid, 20 percent of sodium sulfate, and 15 percent of dextrose, converts it into soft weak fibers. These are stretched and tanned at 50° C. and again at 83° C. by the well-known salt and formaldehyde solutions that have been successfully used for many years

by manfacturers of casein fibers and plastics. The total stretching amounts to about 470 percent. The fiber or yarn collected on the bobbin of the spinning machine is given a final cure or after-treatment with salt and formaldehyde solutions for several hours to improve handling in textile-processing operations. The best fiber was produced when dibutyl tartrate, diglycol laurate, and refined peanut oil were added to the protein-spinning solution and the after-treatment bath contained sodium chloride, hydrochloric acid, and formaldehyde. Sarelon so produced had a dry strength of 0.77 gm. per denier, a wet strength of 0.34 gm. per denier, and dry and wet elongations of 11.8 percent and 22.0 percent, respectively.

### TEXTILE FIBERS MADE FROM CORN PROTEIN

Artificial textile fibers, apparently suitable for blending with other fibers such as rayon, cotton, and wool in knitting yarns and woven fabrics, have been prepared on a laboratory scale from corn protein at the Northern Regional Research Laboratory.

The process includes preparation of a spinning solution by dispersing zein, a fraction of "corn gluten," with caustic alkali, aging the solution for several days, pumping the solution through spinnerettes, coagulating the protein into continuous filaments, and subjecting the filaments to continuous chemical and physical finishing treatments. It is believed that the spinning and finishing of zein fibers can be done continuously on a pilot-plant and industrial scale because the time required for curing and additional finishing treatments is much less than that required for finishing other protein fibers.

Finished zein fiber is strong and resilient and its dry strength is equal to that of wool. Wet strength of the fiber is about half of the dry strength and superior to that of any commercial synthetic protein fiber made thus far. Cleaning the fibers by washing with soap solutions does not damage them.

The textile industry has shown considerable interest in zein fibers, and one company is planning to produce them on a pilot-plant scale.

Further laboratory studies on the preparation of zein fibers, on the continuous spinning and finishing of the fibers in larger quantities, and on their use in yarn and cloth were planned for the succeeding year.

### FEATHERS CONSIDERED POTENTIAL SOURCE OF PROTEIN FIBERS AND PLASTICS

Feathers, like wool and hair, hoofs and horns, and the epidermis of all animals, are composed principally of the fibrous protein keratin, which has physical and chemical properties that make it ideal for protecting animals against injury by exposure to water, wind, sunshine, cold, and harsh contact with the earth, with inanimate objects, and with plants and other animals. In all of its various forms, keratin admirably fulfills the purposes to which it has been adapted in nature, and it is obvious that keratin would be an excellent material for artificial fibers and plastics if its form could be modified in any way desired. Keratin is a cheap raw material; in fact, most of the keratin-containing parts of poultry and other animals killed for food are allowed to go to waste, or are sold at low prices for fertilizer manu-

facture. Chicken feathers are an outstanding example of wasted keratin materials, because in normal times the annual waste of such feathers amounts to as much as 175 million pounds.

With the object of eventually making possible the industrial utilization of feathers and other keratin-containing materials for fibers and plastics, the Western Regional Research Laboratory has conducted fundamental research for several years on the molecular structure and the chemical and physical properties of keratin. Thus far, it has acquired sufficient knowledge for a proper conception of the molecular size of spinnable dispersions of keratin combined with an alkaline salt of an alkylbenzene sulfonate.

During the past year measurements of thermal and mechanical properties of artificial protein fibers gave information concerning the interactions of the molecules and the type of synthesis needed for effective cross-bonding of molecules to attain greater strength in the fibers. Bleached and dyed filaments suitable for some uses, such as the manufacture of wigs for show-window manikins, have been made in the laboratory from chicken-feather keratin. The chief obstacle in the way of using such filaments for textiles is that they absorb water and are much weaker when wet. The knowledge gained in fundamental studies makes possible continued improvement in the wet strength of keratin fibers. When a fiber having sufficient wet strength is developed, it will have many uses and be accepted readily, since satisfactory fibers are in considerable demand.

### CASEIN BRISTLES MOVING TOWARD COMMERCIAL PRODUCTION

In response to the commercial interest in casein fiber as a substitute for natural bristles, last year's research on this product was directed particularly toward evolving a completely continuous process of manufacture. Although design and construction of successful machinery proved time-consuming, it is now possible to carry the fiber much nearer to its finished condition without resort to batch handling. Advantage has been taken of the fact that hardening of the fiber with quinone proceeds more rapidly at 45° C. (113° F.) than at room temperature, the operation being accomplished at the higher temperature while the fiber advances on a new type of automatic reel. By using a reel sufficiently large for the operations, continuous production of casein fiber seems assured. The continuous process is expected to be more economical and to yield a product of somewhat greater uniformity.

One commercial firm has undertaken the manufacture of casein bristles, as developed by the Eastern Regional Research Laboratory, and expects to make trial runs during 1946 as soon as its building is finished and the necessary equipment is installed.

### CASEIN MODIFIED FOR USE IN PLASTICS

The relatively high water absorption of casein and other proteins has limited their utilization as plastics. With the hope of removing this hindrance, and at the same time obtaining material that could be directly converted into finished articles by compression molding, the Eastern Regional Research Laboratory experimented extensively on the chemical modification of casein by combining it with different

kinds of fatty acid radicals, from acetyl ($CH_3CO$—) to stearyl ($C_{17}H_{35}CO$—). All of the products, after being molded into test pieces, showed less water absorption than unmodified casein, but those containing the higher fatty acid radicals were superior to the others with regard to plastic flow, strength, and brittleness. Although as much as 26 percent of higher fatty acid radical could be introduced into the modified casein, it was concluded that the introduction of about 15 percent, together with a final hardening treatment with formaldehyde, yields a molding powder having the best combination of properties. It is believed that the plastic flow of the modified casein can be improved by adding suitable plasticizers, and these are being sought.

Effective plasticizing compounds were found for another type of modified casein, obtained by treating casein with cyanate esters. In this case the use of plasticizer facilitates molding by increasing plastic flow and also permits greatly improved control of the water content of the molded plastic.

## ACONITIC AND ITACONIC ACIDS PRODUCED FROM BYPRODUCT OF CANE-SUGAR MANUFACTURE

A process for the recovery of calcium aconitate from molasses in the course of cane-sugar manufacture was developed by the Agricultural Chemical Research Division to the stage at which it is ready for full-scale commercial operation. During the last cane-grinding season 1 sugar mill produced about 10 tons of the crude salt from a portion of its second, or "B," molasses by simply heating the molasses, allowing the separated salt to settle, and then collecting the salt and washing it with hot water. Another sugar company furnished a sufficient quantity of their "B" molasses to permit continuance of pilot-plant experiments after the 1945–46 grinding season ended, and complete data were obtained for the design of a full-scale aconitate recovery plant which the company expected to operate during the 1946–47 season. This company grinds an average of 3,000 tons of cane per day and plans to recover 2 pounds of calcium aconitate per ton, equivalent to 1½ tons of aconitic acid per day, throughout the grinding season of 90 to 100 days. The recovery operation is to be continuous and automatically controlled, and will return treated molasses to the sugar house at the solids concentration used for further sugar boiling. Maximum recovery will be attained by treating the magnesium-containing molasses with lime and calcium chloride to assure formation of the insoluble dicalcium-magnesium aconitate.

Pilot-plant work was carried out on the liberation of aconitic acid from the crude salt and crystallization of a high grade of the acid for commercial use in the manufacture of plastics. Most of the calcium aconitate produced in the pilot-plant experiments was used in development of a process, on which patents are pending, for converting the crude salt directly to itaconic acid, a substituted acrylic acid useful in manufacturing plastics, by removal of one molecule of carbon dioxide from each molecule of aconitic acid as fast as formed. Fundamental research on reactions of aconitates over a period of several years led to the discovery that aconitic acid is rapidly and smoothly changed to itaconic acid when heated to about 140° C. in solution at

pH 1 to 3 in the presence of calcium ions. A slurry of crude calcium aconitate is treated with the required amount of sulfuric acid and heated under pressure until no more carbon dioxide is evolved. The filtrate from the spent charge yields about one-half pound of itaconic acid crystals per pound of aconitate used. Since yields are lowered by the presence of magnesium in the crude salt, a method was devised for replacing the magnesium with calcium by leaching the partially dehydrated double salt with calcium-chloride solution.

### IMPROVED ACRYLIC RUBBER DEVELOPED

The Eastern Regional Research Laboratory continued its study of rubberlike substances prepared from acrylic esters, which can be made from fermentable carbohydrates through lactic acid as an intermediate. As previously reported, these new rubber substitutes were named "lactoprenes" to indicate their derivation from lactic acid. They are also commonly referred to as acrylic "rubbers." Such rubbers are unusual in that butadiene or similar diene, required for the production of most synthetic rubber, is not used to produce them, and also because they can be vulcanized by an entirely new method based on reaction with chlorine atoms in compounds incorporated with the polymerized acrylic ester. The vulcanized materials endure repeated flexing remarkably well; they have low gas permeability; and they show unusual resistance to enlargement of cuts and to deterioration by oils, oxidation, and aging at normal or elevated temperatures. These outstanding properties, and also the high yields in which acrylic rubbers can be obtained from carbohydrates, suggest industrial possibilities. Almost 1 pound of the finished rubber can be obtained from 1 pound of carbohydrate.

During the last year particular attention was given to development of the type of acrylic rubber called Lactoprene EV. This is prepared by copolymerizing a mixture of 95-percent ethyl acrylate and 5 percent chloroethyl vinyl ether. Pilot-plant studies on polymerization of the mixture dispersed as fine particles in an emulsion showed that it is possible to use as much as 55 parts of unpolymerized mixture to 45 parts of the water emulsion, and to separate the polymerized particles in such a way that they can be washed and dried by commercially feasible methods.

Improved compounding recipes and vulcanizing techniques were developed for Lactoprene EV, and lubricants were discovered which facilitate removal of the vulcanized product from the mold. It was found that the addition of about 8 percent of certain plasticizing oils to the compounded lactoprene before vulcanization causes the product to retain its flexibility and rubbery characteristics at low temperatures.

Several rubber and chemical manufacturers have shown interest in the improved acrylic rubbers and are making evaluation and use studies on them. The material needed for such studies and for investigations on lactoprene in various industrial and government laboratories has been made in the pilot plant of the Eastern Regional Research Laboratory and one of the rubber companies. From the success in pilot-plant operations it appears that lactoprene can be manufactured on a large scale without difficulty.

## CROP RESIDUES USED AS SOFT-GRIT AIR-BLASTING MATERIALS

The report for 1944 told how the Navy had selected ground corncobs, of a certain screen size, as soft-grit material for use with an air blast in cleaning cylinders and pistons of airplane engines after it made comparative tests on various kinds of ground crop residues which were prepared and supplied at its request by the Northern Regional Laboratory as possible substitutes for cracked wheat, corn grits, and clover seeds originally used for this purpose. Later, after testing other similar materials and mixtures supplied by the Northern Laboratory, it adopted a mixture of 60 percent of ground corncobs and 40 percent of whole rice hulls as a soft-grit blasting material for cleaning airplane engines.

The advantage of the soft-grit, air-blast method, in comparison with previously used chemical and mechanical methods for removing carbon and oil residue baked on high compression-engine parts, is that a clean, dry surface is produced without any change in dimensions. This is especially important when the softer alloys are being cleaned.

Recently, various industries have adopted the soft-grit blasting method for cleaning metal surfaces, following demonstrations by the Northern Laboratory which showed how effective it is for removing grease, carbon, scale, and rust from automobile parts and other machinery. Now, soft-grit blasting materials prepared from agricultural wastes are beginning to move into the industrial market.

Several of the large companies that rebuild automobiles have adopted the use of corncob-rice hulls with an air blast for cleaning carburetors, fuel and water pumps, and pistons. Another company solved the problem of cleaning aluminum foundry cores by using this method. A number of glass companies are using the same method for cleaning their molds, and a large oil company is using it for removing paint from the roofs of gasoline storage tanks, since the soft-grit blast material does not produce sparks.

Attention is being given to other agricultural wastes, such as ground fruit pits and nut shells, as soft-grit blasting materials. It is understood that the Army has used ground apricot pits and walnut shells for this purpose.

## BUREAU AIDS STRAWBOARD INDUSTRY FOR BENEFIT OF FARMERS

The strawboard industry, which annually consumes about 750,000 tons of wheat and other cereal straws in 28 mills located for the most part in the North Central States, has recently had difficulty in getting enough straw for its needs. To make up for the deficiency of straw, resulting largely from shortages in farm labor and mechanical equipment for collection, the Northern Regional Research Laboratory has suggested the use of other crop residues such as soybean stalks, flax shives, and sugarcane bagasse, and has aided the industry in developing satisfactory procedures for collecting, storing, and pulping such materials. This service has been largely responsible for the formation of the Fibrous Agricultural Residues Committee in the Technical Association of the Pulp and Paper Industry under the chairmanship

of the man in charge of the Laboratory's pulp and paper section. The technical men and executives of the strawboard industry have met with this committee at the Northern Regional Laboratory, pooling their information and problems, and, under the guidance of the Laboratory's representative, are changing their viewpoint with regard to the industry's relationship toward farmers in the procurement of straw.

One of the most serious obstacles to a sufficient supply of straw for the strawboard industry has been the lack of suitable pick-up balers for use in conjunction with the combine harvester. Although this situation was remedied somewhat by development work on the part of farm implement manufacturers just before the late war, there has been a continued shortage of such baling equipment. The strawboard industry is still not satisfied with the methods of collecting and handling straw for industrial use, and its representatives are collaborating with engineers in two bureaus of the Department of Agriculture's Agricultural Research Administration, with trade associations interested in farm equipment, and with the American Society of Agricultural Engineers and other technical associations in the collective discussion of these problems with the hope of finding a satisfactory solution for them. Prominent executives of the strawboard industry have stated publicly that they are entirely in accord with the viewpoint of the Northern Regional Laboratory and appreciate the work that it is conducting in their field.

An improved process for manufacturing 9-point corrugating board from straw has been developed in the laboratory and is ready for pilot-plant studies. The board made by this process has a tear resistance about 50 percent higher than that of the ordinary 9-point corrugating board and has a larger area per unit weight, which should result in a greater financial return to the manufacturer. Because the pulp drains more freely than that made by the usual lime-cooking process, it should produce more paper on the paper-making machine within a given time. One large mill is attempting to assemble the necessary equipment to carry on large-scale trials of this process.

## NEW PLANT READY FOR SYNTHETIC LIQUID FUELS INVESTIGATIONS

A two-story, factory-type building for housing the semiworks operation under the synthetic liquid fuels project was constructed, and the processing equipment was installed, during the past fiscal year. Some of the equipment has been tested and operated.

As reported last year, this Bureau expects to apply on a semiworks scale a process, previously developed in the Northern Regional Laboratory, for converting the cellulose and hemicellulose constituents of crop wastes into fermentable sugars as a part of the Department's participation in the broad research program for developing synthetic liquid fuels from nonpetroleum sources, authorized by the Seventy-eighth Congress under Public Law 290, April 5, 1944. In collaboration with the Northern Regional Laboratory the sugars obtained in this process will be converted by fermentation into alcohols and other liquid products, which will then be evaluated as motor fuels.

The process under study comprises two steps. In the first step the pentosans are hydrolyzed to xylose with dilute sulfuric acid; in the

second the cellulose is hydrolyzed to dextrose with relatively concentrated sulfuric acid. If the cellulose hydrolysis could be accomplished by the use of dilute instead of concentrated sulfuric acid, a considerable saving in both equipment and acid could be realized. With this in mind, a machine for the continuous high-temperature, dilute-acid hydrolysis of cellulose as well as pentosans has been designed and constructed, and initial experiments with this machine have been made.

Two different sugar solutions are obtained in the process to be used in the semiworks operation. The first is the pentosan hydrolyzate containing primarily xylose, and the second is the cellulose hydrolyzate containing primarily dextrose. Studies on the purification of the pentosan hydrolyzate for use as a fermentation medium have resulted in a method whereby the hydrolyzate, without the addition of auxiliary carbohydrates, can be successfully fermented in good yield to butyl alcohol, acetone, and ethyl alcohol by *Clostridium acetobutylicum*. A method has also been devised for the crystallization of xylose from the pentosan hydrolyzate. The first crop of crystals represents a 62-percent yield of 91-percent-purity xylose. This xylose can be recrystallized to a purity of 97 to 99 percent. The crystalline sugar is being used by the fermentologists of the Northern Regional Laboratory for studies on the frementation of xylose.

Additional fundamental information regarding the reactions involved in producing furfural from the xylose in the pentosan hydrolyzate has been obtained. The reasons for the low yields of furfural obtained by industrial methods are becoming understood, and a method by which consistently high yields of furfural can be obtained is believed to be possible.

Initial studies on the storage and handling of corncobs for processing have been completed. The data obtained indicate that large tonnages of corncobs can be stored outdoors for 6 to 12 months without appreciable decomposition.

## MORE TURPENTINE PLANTS CLEANING PINE GUM

During the past fiscal year the number of turpentine gum-cleaning plants in operation increased to more than 25. Of these, at least two-thirds were licensed by the Secretary of Agriculture to use the patented process developed by the Naval Stores Research Division of this Bureau, while the others use somewhat different processes covered by private patents. An economic advantage of the increase in number of gum-cleaning plants is a corresponding increase in the number of small-scale farmers, with relatively few pine trees, who have access to such a plant and can therefore market turpentine gum as a cash crop. The expansion in gum cleaning also means a larger proportion of perfectly clear rosin in the total production.

## CONTINUOUS PROCESS DEVELOPED FOR DISTILLING PINE GUM

The continuous distilling process intended to replace the present batch process for distilling pine gum has been developed from the pilot-plant stage to plant-scale operation at the Naval Stores Station in Olustee, Fla. The optimum throughput of the continuous still

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appears to be about 4,200 pounds of turpentine-diluted gum per hour at 150 pounds-per-square-inch steam pressure. A smaller-size continuous still has also been built which should be useful as standby equipment and for handling small batches of gum. The smaller still will handle up to 2,000 pounds of diluted gum per hour at 175 pounds-per-square-inch steam pressure and 1,300–1,400 pounds per hour at 120 pounds-per-square-inch steam pressure, which is approximately the same rate as that of the commonly used fire still. With this type of still, the resulting products are the best obtainable from the gum used. The turpentine is clear, containing no entrained gum. The rosin has a satisfactory melting point, and the grades produced are as high as those produced in glass laboratory equipment. The outstanding advantage of the continuous still is that the steam consumption is only about half that required for the batch process.

### SOAP OF MODIFIED ROSIN OR RESIN-ACID COMPOUND USEFUL IN RUBBER-MAKING PROCESS

A new emulsifying agent was developed for use in the preparation of copolymers such as used in the manufacture of GR–S synthetic rubber. This product, the sodium salt or soap of the monomethyl (or ethyl) ester of the addition product of levopimaric acid and maleic anhydride, is easily prepared from pine oleoresin or from esterified rosin. The vulcanizates of the copolymers formed from butadiene and styrene by use of this emulsifying agent showed excellent milling characteristics, with good tack and hardness, and had tensile strengths as high as 4,400 pounds per square inch with elongations of 550 to 700 percent at the break. These values are much higher than the published figures for commercial GR–S rubber.

The present commercial use of a soap of dehydrogenated rosin in the preparation of about 12 to 14 percent of the synthetic rubber produced in the United States necessitates the removal from the rosin of small amounts of retarders that decrease the yield of polymer obtainable within a given time. This can be accomplished with a process, developed by the Naval Stores Research Division, that consists of bringing a solution of the dehydrogenated rosin into contact with a suitable adsorbent such as fuller's earth or magnesium silicate. Laboratory results show that the soap of dehydrogenated gum rosin purified by this process gives a higher polymer yield than do the dehydrogenated rosin soaps now used. The cost of this purified dehydrogenated rosin should be less than that of the product as now made because rosin of lower grade can be used as starting material.

### TURPENTINE CONSTITUENTS MODIFIED BY CHEMICAL PROCESSING

Laboratory experiments by the Naval Stores Research Division indicated that as much as 15 percent of the beta-pinene originally in pine gum may be changed to the less desirable alpha-pinene during the ordinary distillation process when rosin is present. Since the extent of the change depends on the length of time during which the gum is subjected to the distillation temperature, turpentine from pine gum distilled by flash heating in the new continuous still should have an appreciably higher beta-pinene content than that distilled in the

usual manner. Beta-pinene may be separated from turpentine by fractional distillation and is widely used for producing synthetic resins.

A satisfactory substitute for "French fat oil," used in the ceramic industry, was made from the distillation residue of turpentine that had deteriorated to an unmerchantable condition during storage. Preliminary vacuum and steam distillations yielded a considerable proportion of good turpentine.

Further studies were made on the emulsion copolymerization of isoprene, obtained from terpenes, with styrene, particularly with regard to the effect on yield and physical properties of the copolymers produced by varying the ratio of isoprene to styrene, the amount of catalyst, and the amount and type of mercaptan modifier used. Vulcanized synthetic rubber prepared from these copolymers had excellent physical properties.

A new type of reaction between beta-pinene and highly halogenated organic compounds has been discovered. This reaction is effected in a simple manner by gently heating beta-pinene with carbon tetrachloride, for example, for a few hours with organic peroxides as catalysts. The yields of addition products were higher than 90 percent of theoretical in some cases. These derivatives have bactericidal and fungicidal properties and may find uses as germicides or insecticides, in compositions for flameproofing fabrics, as plasticizers for synthetic resins, or as additives for improved lubricating and cutting oils.

## PROGRESS MADE IN DEVELOPING NEW SOURCES OF TANNIN

The increasing dependence of this country's leather industry upon imported vegetable tannins and the more costly synthetic tannins emphasizes the need for developing a more adequate supply of high-quality and moderately priced domestic tanning materials. Further progress toward this end was made by the Eastern Regional Laboratory in its research on canaigre roots, sumac leaves, and scrub oak bark as potential sources of tannin.

*Canaigre roots.*—Field and laboratory studies on the growing and processing of canaigre roots were continued in cooperation with the Bureau of Plant Industry, Soils, and Agricultural Engineering. Harvests from experimental plantings amounted to nearly 12,000 pounds of roots in 1945. Fertilizer requirement studies in progress for 3 years at State College, N. Mex., were completed. Seven fertilizer combinations were applied in replicated plots, and roots were harvested at the end of the first, second, and third years of growth. Yields were increased to a limited extent by the use of nitrogen-containing fertilizers, but not materially by other fertilizers. Average calculated yields per acre per year from plots treated with nitrogen-containing fertilizers ranged from 9.4 to 10.3 tons as compared with 9 tons per acre from control plots. The average tannin contents of roots were increased but slightly by fertilizer treatments.

Canaigre was propagated from New Mexico seed in a 3-year study. Although root yield, tannin content, and purity were low at the end of the first year's growth, they were much improved after 2 and 3 years of growth. The total yield at the end of the third year was equivalent

to 34.4 tons of roots per acre. At the end of the 3 years the calculated average annual yield was 11.5 tons per acre, the average tannin content (moisture-free basis) 21.3 percent, and the average purity 50.5. These results indicate that acceptable yields, tannin content, and purity can be secured by growing canaigre from seed, planting once, and harvesting once in 3 years.

Portions of a 100-pound lot of powdered canaigre roots containing 21.3 percent of tannin were used experimentally to replace quebracho extract in the pretannage of kip side leather and to replace Sicilian sumac or South American tara pods in the retannage of kip leather. The cooperating commercial tanner reported that powdered canaigre root gave results superior to those obtained by either sumac or tara.

Improved laboratory extraction of tannin from canaigre roots was accomplished by pulping the shredded roots to form water slurries at 40°-45° C., using a violent cutting and stirring action provided by a special type of mixer, and subsequently removing solids from the liquors by centrifugal filtration. Tannin recovery by this procedure was about 85 percent as compared with 66, 78, and 80 percent recovery by the previous method applied to shredded, shredded and crushed, and powdered roots, respectively.

For reducing the sugar content of canaigre liquors in order to produce high-purity extracts, seven cultures of bacteria which ferment canaigre sugars in the presence of tannin without appreciably lowering the tannin content were isolated. Four of the cultures used for fermenting liquors and slurries destroyed from 94 to 98 percent of the 10.1 percent total sugars in a sample representing Arizona roots and from 81 to 84 percent of the 20.8 percent total sugars in a sample representing New Mexico roots. After canaigre liquors were fermented with one of these bacteria, extracts of high purity and excellent quality could be prepared from them.

*Sumac leaves.*—In cooperative work by the Bureau of Plant Industry, Soils, and Agricultural Engineering, progress was made in the development of high-tannin strains of domestic sumac. Selected plants have been under cultivation at Beltsville, Md., for several years. Several strains have yielded leaves showing tannin contents as high as 40 percent. These should prove suitable for propagation and initial establishment of high-tannin plantings when commercial growing of domestic sumac is undertaken.

Sheepskin skivers, commercially tanned with Sicilian sumac and three domestic species of sumac, were graded by two sheepskin tanners using pieces of the leather 9 x 12 inches in size. This grading indicated that dwarf sumac (*Rhus copallina*) produced a leather having a "feel" superior to that obtained with the other domestic sumacs and slightly better than that obtained with Sicilian sumac.

Although curing of sumac by artificial drying may be advantageous under certain circumstances, sheepskins tanned in the laboratory with artificially dried domestic sumac were not equal in "feel," when graded by two commercial tanners, to skins tanned with air-dried sumac. This subject is being investigated further.

*Scrub oak bark.*—Because of the irregular size and shape of scrub oak trunks, some type of mechanical debarking appears to be the only economical method of bark removal. Studies along this line, made in

cooperation with the Engineering and Industrial Experiment Station of the University of Florida, involved chipping the entire trunk and large limbs in a hog and separating the bark and wood chips by means of an air-floatation separator. Two 500-pound experimental lots of chips were successfully separated by this method and gave a bark product which could be leached satisfactorily according to a commercial extract manufacturer. Efforts are being made by the Florida cooperators to secure field equipment of suitable size for processing the bark needed for this large-scale test. An economic use for the oak-wood chips is also being sought.

## NEW CHEMICALS MADE FROM NICOTINE

Uses of nicotine and nicotine compounds have been confined almost exclusively to the control of certain insect pests on plants, external parasites on animals, and, to a small extent, internal parasites of animals. In research on additional outlets for the industrial utilization of tobacco, the Eastern Regional Laboratory prepared new chemicals from nicotine which may find uses in other fields. Some of these chemicals, classed as beta-substituted pyridine derivatives and including beta-ethyl pyridine, beta-vinyl pyridine, beta,beta-dipyridyl, nicotyrine, and myosmine, are produced when nicotine is decomposed by heat in the presence of siliceous contact materials.

Myosmine, in particular, is of interest, because it is an alkaloid that has never been found ready-formed in plants. It was previously known to be present in cigar smoke, and was believed to be formed from nicotine while the tobacco burned, and to contribute markedly to the pleasant taste and aroma of cigar smoke. A substantial quantity of myosmine was prepared in the laboratory, and samples were sent to 25 tobacco companies for evaluation as a tobacco adjunct. Two firms reported that the addition of myosmine improved the quality of their products. Although the tests have not been concluded, it appears that the effect of myosmine is more pronounced in pale flue-cured tobacco than in blends containing darker varieties of tobacco.

The chemicals obtained by decomposing nicotine with heat were used in synthesizing other chemicals. Some of the synthesized compounds, as well as the starting materials, were supplied to drug companies for evaluation tests. Several showed promise as chemotherapeutic agents and provided valuable clues for further studies. One of the synthetic compounds, dithiodinicotyrine, showed some antimalarial activity.

## LARGE COMMERCIAL SWEETPOTATO-STARCH PLANT STARTS OPERATIONS

Shipment in December 1945 of the first carload of sweetpotato starch from the new factory at Clewiston, Fla., marked another milestone in the advance of southern agriculture and industry. The new starch plant and associated facilities, modern and well equipped in every respect, will afford an outlet for sweetpotatoes from 12,000 or more acres annually; the domestic supply of high-grade root starches for food and industrial applications will be augmented by 50 million pounds or more a year; and some 20 million pounds or more a year will be added to the supply of carbohydrate feed for southern livestock.

This development in the manufacture of starch from sweetpotatoes is the outgrowth of over 15 years of research and development work in this bureau. The proving ground for the processes employed was the Laurel Starch Factory, owned by a farm cooperative, which operated for 10 years, through 1944, with technical advice and assistance from the chemists and engineers of the United States Department of Agriculture. Thus, the year-by-year progressive acquisition of new data and experience in laboratory, pilot-plant, and factory investigations of production and processing of sweetpotato starch, with evaluation of the characteristics of the product, has provided the foundation for recent and potential future developments of sweetpotato-starch manufacture as a southern industry.

Under the cooperative agreement between the Department of Agriculture and the United States Sugar Corporation for mutual assistance in promoting industrial utilization of sweetpotatoes, chemists and engineers of the Southern Regional Laboratory gave technical advice and assistance during the test runs at the new plant, in the operation and adjustment of the processes and equipment for washing, shredding, grinding, screening, centrifugal purification, bleaching, dewatering, and drying. Particular attention was given to setting up methods and procedures for chemical control of processing, with application of the improved technique and equipment as developed in the Laurel Starch Factory. These included the method for adjustment and control of pH and lime-water proportion, the rapid hypochlorite-dispersion method for determination of starch in sweetpotatoes and in pulps, rapid and accurate procedures for determination of moisture in finished starch, and other chemical methods for analysis of sweetpotatoes in the different stages of processing.

Because of continued demand for dehydrated sweetpotatoes to meet military, and later UNRRA, requirements, Sweet Potato Growers, Inc., at Laurel, Miss., suspended production and processing of sweetpotatoes for starch during the 1945–46 season and concentrated all efforts on dehydration of sweetpotatoes and production of sweetpotatoes for the fresh-food market. Technical advice and assistance to this cooperative were rendered by the Southern Regional Laboratory in connection with dehydration. A continuous rotary preheater was designed for elevating the temperature of the sweetpotatoes before peeling in order to reduce discoloration from enzymic oxidation. With installation of equipment of this design at the Laurel plant, blackening was practically eliminated, and the former bottleneck at the trimming table was removed. At the termination of operations in January 1946, the Laurel plant had turned out about 1,350,000 pounds of excellent product, with a trim loss of only 4.4 percent (due almost entirely to ends, a few cuts and bruises, and a few light-colored potatoes) and a peeling loss of but 8.25 percent.

Research was continued on the coagulation and concentration of the crude protein in sweetpotato-starch fruit water and on production of feed yeast (*Torula utilis*) from the sugar in the effluent, the processes being applied in pilot-plant operations with equipment designed in the Southern Laboratory and erected in its pilot plant at New Orleans. The equipment for yeast production was designed and assembled with the expectation that it would be dismantled, moved, and re-erected at a commercial plant for operation under actual factory conditions.

Preliminary batch runs were made with sweetpotato extract as the nutrient medium to test mechanical functioning. Loss through foaming was excessive in the larger-scale propagators, and a number of substances were tested to determine their effectiveness as antifoam agents and their toxic effect on the yeast organism. The problem was apparently solved by redesign of the piping system connecting the propagators. The complete equipment was erected in a Florida citrus cannery, and feed yeast was produced in experimental runs with press liquor in order to evaluate the production of feed yeast as a method of solving a waste-disposal problem.

### STARCH AND SIRUP MADE COMMERCIALLY FROM WHEAT FLOUR

When it became apparent during the recent war that the potential supply of corn sirup was not enough to completely offset reductions in the supply of cane sugar, the Northern Regional Research Laboratory started an investigation on the possibility of producing starch from wheat or wheat flour and using this starch, like cornstarch, for the production of glucose sirup. The so-called batter process for separating starch and gluten from wheat flour was developed, and this process was recommended for use in idle beet-sugar factories, after slight alterations in the equipment, for the preparation of a concentrated starch suspension and the conversion of this starch suspension into glucose sirup. Taking a typical beet-sugar plant with a capacity of 1,000 tons of beets per day as the basis for calculations, it was estimated that the altered plant could process 144,000 pounds of moisture-free flour per day with a daily yield of 148,300 pounds of glucose sirup, having a gravity of 43° Baumé, and 29,700 pounds of denatured gluten, containing 3 percent moisture. Before the end of the war one commercial firm used the batter process on a large scale in a beet-sugar plant and converted the starch suspension into sirup.

Industrial interest in this process increased during the past year because of the continued scarcity of sugar and other sweetening agents. Several companies made small-scale tests with the process after visiting the Northern Laboratory, and some undertook to produce wheat starch and gluten commercially. New applications of the process have been primarily for the production of alcohol and glucose sirup from the starch. Recent commercial production is reported to be approximately at the following annual rates: Dextrose sugar and glucose sirup, 150 to 200 million pounds; high-protein wheat gluten, 20 to 30 million pounds; industrial alcohol, more than 5 million proof gallons. Plans for new large-scale application of the process have been reported.

### CHANGE IN STEEPING METHOD AIDS RECOVERY OF STARCH FROM MOLDED CORN

In 1944 and 1945 much of the corn planted late, because of continued wet weather and floods, did not reach full maturity before the first killing frosts. This corn had high moisture content when harvested and it dried very slowly. Considerable quantities of such corn molded because it was too moist when put in storage. The damaged corn was not good for feeding, so it was offered to corn

processors for use in the manufacture of starch and starch products. Since the corn processors had trouble in separating the starch from the protein of molded corn, and some of them appealed to the Northern Regional Laboratory for information and advice, steeping studies were made to learn the cause of the trouble.

The processors had reported that the yields of starch were low because the starch granules did not settle properly from their suspension in water, and that the starch was of poor quality, containing more protein than was normal and having a bad color and low viscosity value. The results of the laboratory studies confirmed these observations and also showed that excessive quantities of starch and protein were retained in the fiber fraction. It was found that molded corn requires less steeping than sound corn to soak up the same quantity of water, but that water content alone does not determine the ease of separating starch from the other constituents. Because part of the starch was decomposed it was impossible to obtain high-quality starch from badly molded corn by any method tried. However, starch of good quality could be obtained in satisfactory yields from moderately molded corn under certain conditions.

A low concentration of sulfur dioxide is always added to the water used for steeping corn for wet milling, because it softens the protein network, disperses some of the protein, bleaches the starch, and promotes absorption of water by the grain. In the laboratory studies it was found that in moderately molded corn the protein is more resistant to the action of sulfur dioxide than that of sound corn, but in badly molded corn the protein is easily dispersed by the sulfur dioxide because it has been already largely broken down by the action of the mold enzymes.

On the basis of these observations the sulfur dioxide treatment for moderately molded soft corn was made somewhat more drastic than that commonly used for sound corn. This could be done by increasing the sulfur dioxide content of the steep water or by prolonging the steeping time with the usual concentration of sulfur dioxide in the steep water. It was found that the separation of starch was aided in both ways. About the same results were obtained by steeping 72 hours in water containing 0.1 percent sulfur dioxide as by steeping 20 hours in water containing 0.1 percent sulfur dioxide and 4 hours in water containing 0.3 percent sulfur dioxide. Both steeped samples yielded starch of good quality, whereas some of the same corn steeped for 24 hours in distilled water without sulfur dioxide gave a tan-colored starch with a musty odor. The starch recovery after the sulfur dioxide steeps was about twice as high as after the water steep.

In view of these results some corn processors raised the sulfur dioxide content of the steep water during the last few hours of steeping molded corn and obtained beneficial results. Such modification of the usual processing method made it possible for the wet millers to produce much needed commercial starch and starch products from corn that was unfit for food products or feeding of livestock.

### PILOT PLANT PLANNED FOR POTATO STARCH

Representatives of the Eastern Regional Research Laboratory investigated the status of potato-starch manufacture in Maine and the different types of equipment in current use. The information

obtained will be used for chemical engineering studies preparatory to setting up an integrated pilot plant at the Eastern Regional Laboratory for experimental production of white potato starch with the purpose of improving yields and quality of product as well as reducing stream contamination.

## NEW METHOD FOUND FOR FRACTIONATING STARCH

The common kinds of cereal and root starches are known to be mixtures of essentially two carbohydrate substances which, although of the same elementary composition, have somewhat different chemical and physical properties and are therefore considered to have different kinds of molecules. One of these substances, amylose, appears to have linear molecules similar to those of cellulose, a fibrous constituent of plants. The other, amylopectin, appears to have molecules branched like those of pectin, a jelly-forming substance obtained from plants. The common starches contain from 20 to 30 percent of amylose and from 70 to 80 percent of amylopectin.

Believing that amylose, because of its linear molecules, would yield an acetate and other chemical derivatives suitable for the production of synthetic fibers and plastics, the Northern Regional Research Laboratory has attempted to develop a practical commercial process for isolating amylose from starch or for fractionating starch to obtain a fraction that is principally amylose. On the basis of the conditions and chemical agents used in the different known laboratory methods of fractionating starch, a general working hypothesis was devised to explain the mechanism of starch fractionation, and this hypothesis aided in the development of a new starch-fractionation process which is believed to have commercial possibilities.

The process is based on the ability of amylose to form complex chemical compounds with long-chain fatty acids. The first step of the process consists in heating a slurry of corn starch and water, to which a little oleic, stearic, or other fatty acid has been added, under pressure to get a clear starch paste. This paste is held at a temperature of 90° C. (194° F.) for 24 hours or more, during which time crystalline particles of amylose-fatty acid complex separate and settle to the bottom of the container. The clear paste is then syphoned or poured off, and water is removed from the precipitated complex by centrifuging the mass and washing it with anhydrous ethyl alcohol. The fatty acid can be removed by subjecting the complex to repeated extractions with 85-percent methanol, leaving a residue that is about three-fourths amylose and one-fourth amylopectin. If one desires to recover amylopectin, it can be precipitated from the clear starch paste, after removal of the amylose, by pouring the paste into anhydrous ethyl alcohol.

Preliminary results obtained in pilot-plant experiments with the starch-fractionation process indicated that preparation of the clear starch paste might be made continuous. However, further work on this operation is necessary before proceeding with pilot-plant studies of the other steps of the process.

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## ENZYME RESEARCH YIELDS INTERESTING FACTS

Results having both scientific interest and practical value were obtained in further studies of beta-amylase, one of the two diastatic enzymes that make malt useful for converting starch to fermentable sugars. It was reported last year that the addition of extra beta-amylase to western barley malt, which has low diastatic value, brings its diastatic value quite up to that of eastern barley malt, and that sweetpotato press juice or an extract of wheat flour made by treatment with a dilute sulfite solution could be used as the source of extra beta-amylase. A survey of many agricultural commodities failed to discover any other as rich in beta-amylase as the sweetpotato, and Porto Rico Red was the richest source of beta-amylase among the sweetpotato varieties tested.

Beta-amylase from sweetpotato juice was finally obtained in the crystalline form. The crystals have scientific value as a pure enzyme for use in further study of starch structure and enzyme action. They represent the first protein obtained in crystalline form that has diastatic activity. Their starch-conversion power is enormous, being several thousand times as great as that of dry malt. They can be of practical value in any process where starch must be rapidly split to sugars without introducing a large amount of extraneous material.

The Enzyme Research Laboratory had previously foundthat wheat contains almost as much beta-amylase as there is in malt, but that it becomes active only after special treatment, as with sulfurous acid or sulfite solution. A recent study of the occurrence of beta-amylase in the growing wheat seeds showed that the active enzyme is formed rapidly during the early dough stage and then becomes inactive as the wheat ripens. The enzyme is also present in the inactive form in wheat flour, but it can be activated by special treatment.

Since the ripening of citrus fruits and their behavior during storage are governed in large part by the action of little known or unknown enzymes, a study of the enzymes in citrus fruits, particularly in oranges, was started at the suggestion of the Joint Problems Board of the Citrus Industry. Several enzymes, previously not known to occur in citrus fruits, were discovered in oranges, and one of them, a phosphatase, appears to be connected with changes in the acid and sugar contents during ripening. Since the phosphatase in orange juice is destroyed gradually by heat, the amount of the enzyme present can be used as a test to regulate pasteurization. Studies on the respiration of oranges indicated that considerable amounts of substances not yet recognized may accumluate in the peel of oranges during cool storage.

## MALT REPLACED BY SPENT LIQUOR FROM MOLD CULTURE

In an attempt to find sources of starch-converting enzymes that can completely replace malt, a survey was made by the Northern Regional Research Laboratory of enzyme production of 250 molds cultured in thin distillery slop. Several mold strains were found which form significant quantities of enzymes, and these enzymes are being employed in fermentation studies. One mold in particular, a strain of *Aspergillus niger*, produces unusual quantities of amylase

and maltase, and culture filtrates from this organism can totally replace malt in the yeast fermentation of corn when used in a method developed at the Northern Laboratory. It was found that a very satisfactory medium for the propagation of this mold can be prepared by the addition of as little as 1 percent of ground corn and 0.5 percent of calcium carbonate to thin distillery slop. When the mold is grown on this medium the enzyme activity of the liquor reaches a high level in 3 days. The first experiments indicated that 20 gallons of such liquor were required to convert the starch in 100 gallons of cooked grain mash to fermentable sugars at the recommended conversion temperature of 130° F. Many mashes were converted and subsequently fermented to alcohol with an average yield of 5.25 proof gallons per bushel of corn containing 12 percent moisture. The highest yield was 5.40 proof gallons. Later, the conversion temperature was raised to 140° F. and the proportion of liquor used for conversion was reduced first to 15 gallons, then to 10 gallons, and finally to 7 gallons, per 100 gallons of mash, with satisfactory results. Fermentations were complete and usually required 48 to 60 hours.

It was found that the yields of alcohol from the fermentation of grain mashes converted with 10 percent malt or with a liquor containing the mold enzymes are comparable. There are indications that fermentations in which mold enzymes are the starch-converting agents give a slightly higher yield of alcohol—about 0.1 proof gallon more per bushel—than is obtained with malt.

### MOLD-FERMENTATION RESIDUE USEFUL AS FEED

The Northern Regional Research Laboratory found that the mold *Penicillium chrysogenum* synthesizes significant amounts of several B-complex vitamins while it is producing penicillin in the submerged fermentation process. This knowledge has aroused considerable interest in the nutritive value of the fermentation residue, since recovery of the residue for feed would ease a serious waste-disposal problem. Therefore, some of the fermentation residue was dried and submitted to the Bureau of Animal Industry for use in feeding tests to determine its value as an adjunct to poultry rations. The report showed that the dried product, when fed at a 3-percent level to growing chickens, supplied enough riboflavin to prevent "curled-toe" paralysis and to support as good growth as could be obtained with similar basic feed containing 0.6 percent of butyl-alcohol fermentation solubles. The dried penicillin-fermentation residue was also fed at a 6-percent level with favorable results in growth and health of the chickens. These results show that penicillin residue may be an efficient source of animal feed and that it does not contain toxic substances.

### CITRUS PROCESSING WASTE USED TO PRODUCE BYPRODUCT FEED YEAST

Laboratory experiments and brief commercial production have demonstrated that torula yeast can be grown on citrus-waste press liquor, but the process has not become established commercially, and disposal of this waste from the citrus-pulp feed mills continues to be an onerous and costly problem. A similar possibility exists in handling waste press liquor from sweetpotato-pulp feed, and the Sweet-

potato Products Division of the Southern Regional Research Laboratory had constructed a pilot plant for investigation of a continuous yeast-propagation process. Industrial use of the process with either citrus waste or sweetpotato waste press liquor is awaiting demonstration on a sufficiently large pilot-plant scale to determine costs of operation, yields in continuous production, and effectiveness in mitigating the disposal problem. Production of enough yeast to establish markets and value of the product is also an essential in economic evaluation of the process.

A large citrus cannery in Florida, having a byproduct-feed mill that discharges over 20,000 gallons per day of press liquor, offered its facilities for conducting the experimental work of yeast production on an adequate scale. The Agricultural Chemical Research Division and the Sweetpotato Products Division cooperated with the firm in this work under a formal memorandum of understanding. The complete pilot plant was moved to the cannery before the end of the last processing season, and it was operated 24 hours per day for periods of 5 to 12 days continuously. Citrus molasses (made by concentrating press liquor) was used to maintain the yeast culture and carry on the operation over week ends when the feed mill was not operating, but most of the experiments were on press liquor from the commercial plant. Different rates of aeration were tried in continuous fermentation with rates of influx and efflux varying from 50 gallons per hour to 200 gallons per hour. A modification of the equipment overcame foaming, and it was demonstrated that the culture of torula can be maintained substantially free from contamination for long periods. A continuous centrifuge was successfully used to concentrate the yeast, some of which was dried on a small drum drier. Larger quantities were incorporated with the citrus-pulp feed before being dried. The sugar content of the liquor was reduced from 5 percent to 0.2 percent or less in the fermentation, and the biological oxygen demand was reduced to one-fourth that of the unprocessed liquor.

The waste press liquor from the feed mill contains about 5 percent carbohydrate (mostly sugars) and amounts to about 2,000 gallons per ton of pulp feed produced. Theoretically, it is possible to produce at least 300 pounds of dry yeast from this amount of liquor which, if incorporated in the feed, would yield 2,300 pounds of product with a 12-percent protein content. The same amount of cannery waste now produces 2,000 pounds of feed containing only 6 percent protein. Yeast dried separately and sold as such may bring a higher price. This will be determined by submitting samples to potential users. Longer continuous operation of the pilot plant is planned for the 1946–47 season to produce larger quantities, to determine power, heat, labor, and other costs accurately, to learn minimum effective quantities of nutrients that must be added, and to perfect control of the process details in order to design a full-scale plant.

### VEGETABLE WASTES RETTED TO CONCENTRATE PROTEIN AND CAROTENE

The Eastern Regional Research Laboratory prepared plant material of increased protein and carotene concentration by applying anaerobic fermentation with *Clostridium roseum* (essentially a controlled retting

process) to blue grass, alfalfa, and leafy vegetable wastes including bean and pea vines, carrot, turnip, and beet tops, and lettuce and broccoli trimmings. The walls of the individual plant cells of the blade portions of the leaves were digested by the bacteria or the enzymes produced by them, and the contents of the cells were released as separate particles called protoplasts. These were readily separated from the unaffected residue of leaf stems, ribs, veins, and cuticle by screening and washing.

The dried protoplasts contained from 31 to 56 percent of protein, 18 to 26 percent of fatty substance, and 0.04 to 0.20 percent of carotene, thus representing a two-fold to seven-fold increase in concentration over the original leaves. When the fatty substance was removed by extraction with a solvent, the protein content of the dried residual material was 84 percent for broccoli, 58 percent for lima bean leaves, 52 percent for beet tops, and 37 percent for carrot tops.

The same fermentation process was applied to food-storage tissues of plants, including the taproots of carrots, sweetpotato tubers, and the flesh of winter squash. In these cases, separate protoplasts were not observed after the fermentation, but a comparable fraction of pasty material was obtained. This fraction from carrots, when dried, contained 2.2 percent of carotene (provitamin A), which is unusually high.

The use of a retting process for concentrating certain fractions of vegetable wastes was suggested by the promising results previously obtained in the Emergency Rubber Investigations when such a process was used as a pretreatment for cryptostegia leaves to facilitate recovery of their rubber contents. Since the fractionation of the leaf materials and the recovery of protoplasts and their water-insoluble constituents were so satisfactory, it was thought advisable to apply the fermentation process to leaves of other plants and to other kinds of plant tissue. From the results obtained thus far, it appears that with this process it will be possible to prepare concentrated fractions of plant material for use as high-protein feed supplements or for the extraction of carotene, tocopherol, or other plant components.

### FRUIT AND VEGETABLE WASTES USED TO PRODUCE FEED AND MEDICINE

Successful small-scale production of a feedstuff from torula yeast grown on pear waste indicates that its commercial manufacture may soon be feasible. Some problems encountered in preparing the waste for fermentation and in converting the unfermented residue to a salable byproduct remain to be solved. Headway has been made in solving these problems, and the investigation will continue. In the West, where protein feeds are always short, this additional source of protein feedstuff would be a boon to livestock growers and feeders.

The prominent role of antibiotics in modern medicine has stimulated interest in subtilin, an antibiotic named and developed by the Western Regional Research Laboratory. The bacterium that produces subtilin is grown on a medium prepared from asparagus wastes. Although the medicinal use of subtilin awaits the outcome of medical research, the results of bacteriological studies warrant the hope that this substance will be useful in the battle against tuberculosis and

amoebic dysentery, diseases that have resisted the effects of other medicaments. The Western Regional Laboratory has continued to supply the heavy demand for experimental quantities of subtilin and has succeeded in increasing several times the production of subtilin from asparagus juice by both the tray or surface culture of the organism and its submerged culture. Evaluations through chemical reactions and biological effects on animals have been made by the Laboratory and cooperating agencies with extremely encouraging results. Since subtilin may have antibiotic value against plant diseases, particularly those caused by fungi, samples for experimental use have been supplied to most of the plant pathologists engaged in research at the experiment stations of the various western states.

### TOMATIN AND OTHER ANTIBIOTICS FROM PLANTS HINDER GROWTH OF PARASITIC FUNGI

During the year intensive investigations were continued, in cooperation with the Bureau of Plant Industry, Soils, and Agricultural Engineering, to isolate and identify biologically active compounds from green plants with particular attention to compounds possessing antibiotic activity toward the micro-organisms that cause plant diseases. In the report for 1945 it was stated that tomato plants had been found to contain an antibiotic substance capable of inhibiting the growth of *Fusarium*, the fungus that is responsible for a common wilt disease in the tomato. This antibiotic agent, which was named "tomatin," was found to be present in about the same proportion in all of the commercial tomato varieties examined, whether these varieties are susceptible or resistant to the wilt fungus, provided the plants are not infected with the fungus. In the case of infected wilt-susceptible plants, tomatin diminishes as the disease progresses, until it can no longer be detected in completely wilted plants. In the case of infected wilt-resistant plants, however, tomatin is maintained at normal levels, and wilting does not occur. In view of these and other confirmatory results it was concluded tentatively that the growth of *Fusarium* within the plant is responsible for the disappearance of tomatin and, conversely, that tomatin is at least one of the factors responsible for the resistance that some tomato varieties offer to the wilt-producing fungus.

While the occurrence of antibiotic agents in green plants is by no means general, it has been demonstrated that several plants other than the tomato contain antibiotic agents possessing tomatin-like activity. The leaves of cabbage, potato, sweetpotato, and chili pepper plants contain substances that, like tomatin, strongly hinder the growth of the wilt-producing *Fusarium* fungus in culture media. The significance of the presence of antibiotic agents in these plants, from the standpoint of their resistance to disease, is being investigated.

It has also been demonstrated by laboratory cultures that tomatin is even more effective in hindering growth of certain bacteria and fungi that cause human and animal disease than it is in hindering the growth of the tomato-wilt fungus. Tomatin is most active against cultures of fungi that cause skin diseases and several of the yeast-like fungi that cause serious internal diseases. For this reason, tomatin, if found to be effective and safe for clinical use, may supplement such well-known antibiotic agents as penicillin and streptomycin, which

are completely without effect upon the disease-producing fungi. Preliminary toxicity tests with guinea pigs indicated that animals can tolerate the internal administration of moderately large quantities of tomatin without fatal consequences, although unfavorable reactions are produced with the impure preparations that are now available. Work upon this phase of the project is being intensified, inasmuch as medical research during the past several years has shown serious fungus infections not only among returning veterans but also in the civilian population. Improved diagnostic methods have shown fungus infections to be much more prevalent and widespread than was supposed heretofore. The medical profession has no safe and effective method of combating the more serious fungus infections. If current investigations culminate satisfactorily, tomatin or one or more of the antibiotic agents shown to be present in certain other plants may be used for this purpose.

Investigations involving the synthesis of new substances that regulate plant growth were initiated during the year for the purpose of determining the mechanism of their action and the chemical groups responsible for their effects upon the metabolism of the plant. Forty-three organic compounds were prepared and tested on plants in cooperation with the Bureau of Plant Industry, Soils, and Agricultural Engineering. While the results of these tests have been promising, too few compounds have been tested to permit the drawing of any conclusions or to show any correlations between chemical structure and hormonal activity toward plants. The information gained thus far is being used to advantage in guiding further research.

## DRUG FIRMS MAKE RUTIN FOR CLINICAL TESTS

It was reported last year that the Eastern Regional Laboratory had found buckwheat plants to be a practical source of the new drug rutin (which it had previously extracted from flue-cured tobacco) and had developed methods for extracting rutin from green buckwheat leaves or the dried leaf meal and purifying it for medicinal use; that 20 pounds of rutin had been prepared in a pilot plant and supplied to more than 100 physicians and pharmacologists for experimental use; that clinical evidence of the therapeutic value of rutin continued to accumulate; and that several drug manufacturers planned to begin the commercial production of rutin in 1945.

During the summer of 1945 about 300 pounds of rutin were extracted from green buckwheat plants by four drug manufacturers with technical guidance by chemists of the Eastern Regional Laboratory. This rutin was not put on the market, but was used by the firms' research staffs and supplied in tablet or capsule form to interested physicians for experimental use. By the end of the fiscal year, clinical studies on the therapeutic value of rutin for relieving various pathological conditions of the circulatory system had progressed to such an extent that papers were being prepared by several physicians for publication in medical journals. Reports from some of the clinical tests indicated that rutin reduces the tendency of the capillary blood vessels to rupture with consequent hemorrhage in some persons having high blood pressure and that rutin retards the progress of diabetic retinitis.

Two physicians of the University of Pennsylvania Medical School, which is conducting collaborative clinical research on rutin, planned to demonstrate its medicinal use at the 1946 annual convention of the American Medical Association.

The Eastern Regional Laboratory developed a spectrophotometric method for the quantitative determination of rutin in crude and medicinal preparations, and also of the quercetin formed by hydrolysis of the rutin. As a result of pilot-plant experiments, the Laboratory improved the processes for extracting and purifying rutin from green and dried buckwheat and made details of the processes available to manufacturers.

Two new processes, developed on a pilot-plant scale, for extracting rutin from dried buckwheat leaf meal will make it possible for rutin producers to buy the meal already prepared and operate throughout the year instead of only during a short season when fresh, immature buckwheat plants can be harvested. The production of buckwheat leaf meal for the drug trade could, in many cases, be carried out profitably by the producers of alfalfa leaf meal with their present drying equipment. In one of the new processes the crude rutin is extracted with boiling water, alcohol being used only in the purification step. The volume of alcohol tied up in the process, and continuously recovered for reuse, is about 17 gallons per pound of rutin in course of production, as compared with about 128 gallons of alcohol per pound of rutin when alcohol is used as the extracting agent.

The drug companies extracting rutin found that the product was contaminated with iron or copper when iron or copper equipment was used. Studies in the Eastern Regional Laboratory confirmed the possibility of the formation of metallic complexes with rutin, when hot rutin solutions come in contact with iron or copper, and suggested means for avoiding or removing contamination of rutin by such metals.

Some of the reports on physiological effects of rutin were confirmed by the results of experiments with laboratory animals by the Bureau's Pharmacology Laboratory. Other pharmacological studies in progress in this bureau and in the University of Pennsylvania Medical School are aimed at the development of a biological assay of rutin preparations. When such a method has been developed and sufficient experimental evidence has been obtained, through biological experiments and clinical tests, to establish that rutin has therapeutic value and is safe for internal medication, it will be possible for drug firms interested in producing rutin to take the necessary steps to have it recognized officially as a new drug, after which it can be put on the market.

It was expected that 12 or 15 drug firms would be engaged in the small-scale production of rutin in 1946 and that somewhere between 10,000 and 20,000 pounds would be manufactured. The higher figure would require about 4,500 tons of fresh buckwheat plants or an equivilant quantity of dried buckwheat leaf meal.

## PROGRESS MADE IN RESEARCH ON CHEMISTRY AND IMMUNOCHEMISTRY OF OILSEED ALLERGENS

Last year's report indicated that the allergenic component of the natural proteose (designated 1A fraction) of castor beans comprises more than two distinct protein substances which are closely related in chemical composition and therefore difficult to separate in homogeneous form.

Previous attempts to obtain a homogeneous protein substance from the 1A allergenic fraction of castor beans by fractionation with ethyl alcohol in the presence of various buffers were unsuccessful, because much of the allergen was lost in the fractions of lower solubility. Therefore, it was necessary to develop a new large-scale fractionation procedure which is similar in principle to the separation of a dissolved substance by distribution between two immiscible solvents. Numerous fractions were obtained by this procedure supplemented by precipitation of the protein with picric acid. Other fractions were obtained by prolonged dialysis, in which the separation is dependent upon differences in molecular size of the component proteins.

Seventy-seven fractions obtained from the 1A allergenic fraction of castor beans were analyzed and tested for homogeneity by solubility measurements. The first fraction contained 39.7 percent carbohydrate and 12.5 percent nitrogen, and the last fraction, representing the most highly purified stage, contained 0.37 percent carbohydrate and 19.1 percent nitrogen. There were corresponding advances toward homogeneity of the purified fractions with improvement becoming more gradual after many separations. The last fraction was still not perfectly homogeneous.

The experience gained in the fractionation of castor-bean allergen indicated that the new procedure was worthy of further trial and that ultimate success in obtaining a pure allergen from castor beans might reasonably be expected by starting with a large quantity of 1A allergenic fraction. Accordingly, the preparation of a sufficiently large quantity of fraction 1A from castor beans was undertaken.

Three different lots of commercial castor bean pomace, totaling more than 500 pounds, were processed to obtain the 1A allergenic fraction, the yields of which were about 0.18, 0.26, and 0.31 percent. The 1A fractions from the two lots giving the higher yields will be combined and used in fractionation experiments on a larger scale. The 1A fraction from the other lot was not only proportionately less, but also higher in carbohydrate content and substantially lower in allergenic activity than corresponding fractions from the other two lots, and for that reason will not be added to the others.

The allergen from castor beans differs from other allergens isolated thus far from oilseeds in that it does not contain the amino acid tryptophane. Since fraction 1A from castor beans is as potent as any of the allergens studied, it has been concluded that tryptophane is not necessary for the allergenic and antigenic properties of the natural proteose type of allergen represented by 1A fractions. The

validity of this conclusion depends upon the accuracy of the method used for determining tryptophane. The dependability of methods for the quantitative determination of this amino acid in proteins has long been a controversial subject, and experience in the use of currently available methods indicated the need for a critical reexamination of this problem. During the year, therefore, a study was made of the color-forming reaction between tryptophane, paradimethyl aminobenzaldehyde, and sodium nitrite, and an improved procedure was developed for the quantitative determination of tryptophane in proteins.

New allergenic fractions were separated from Barcelona and DuChilly filbert nuts. This is of special interest because about 36 percent of the nitrogen in them is in the form of the amino acid arginine. This is a higher proportion of arginine than has been found in corresponding fractions from most of the oilseeds.

When an animal is sensitized to a particular foreign protein by having a small quantity introduced into its blood stream, that animal, after a suitable incubation period, will suffer a shock, varying from mild to fatal, when the same protein enters its blood stream a second time. This reaction, known as anaphylaxis, has often been used with guinea pigs to identify proteins, but its use for quantitative estimation of proteins has been limited. Adaptation of this remarkably specific reaction to quantitative determinations would increase its value for guiding chemical fractionation of complex mixtures of naturally occurring proteins. However, since the effects of variable factors, such as age of experimental animal, size and route of sensitizing dose, and size and route of challenging dose, have never been adequately determined, the use of this reaction for the quantitative measurement of proteins has not been feasible. During the past year a study of the effects of individual variables was made in connection with the investigation of allergens of oilseeds. From this study it was concluded that, when variables influencing the degree of anaphylaxis are strictly controlled, quantitative estimations of antigenic activity of individual proteins can be made with the same accuracy as determination of the potency of poisons.

## PHARMACOLOGY LABORATORY AIDS VARIOUS UNITS OF AGRICULTURAL RESEARCH ADMINISTRATION

During the past year the Bureau's Pharmacology Laboratory has been called upon by all of the four regional research laboratories and by the Bureau of Plant Industry, Soils, and Agricultural Engineering to aid in the investigation of certain substances for toxcity or other biological effects in cases where such substances were being considered for use as foods or drugs or could be present in foods or drugs either naturally, or as additions, or as contaminants from packaging materials, chemical processing, or processing equipment.

Work for the Western Regional Laboratory on the antibiotic citrinin was completed, and a paper on the biological effects of this mold-produced substance was prepared for publication. It was found that citrinin, which suppresses the growth of certain bacteria, has physiological effects similar to those of pilocarpine and acetylcholine.

This knowledge lays the foundation for studies on the possibility of using citrinin in veterinary medicine.

Intraperitoneal implantation of the ammonium salt of gluten sulfate in rats did not cause any toxic reaction. Gluten sulfate, produced from wheat gluten by the Western Regional Laboratory, has exceptional absorptive properties, and for that reason it is being considered as a possible dry dressing for wounds and burns.

Studies on the chronic toxicity of Norelac, a water resistant and fusible resin developed by the Northern Regional Laboratory and considered as a suitable coating for paper and fiberboard to be used for waterproof and heat-sealing food packages, showed that this substance is harmless, as judged by the growth curves of albino rats consuming it in their diet over a long period.

The potassium salt of saccharic acid, produced from corn sugar by chemical processing at the Northern Regional Laboratory, was found to be unsatisfactory for powdering surgical gloves. Unlike acid potassium tartrate, which is used for this purpose, the saccharate salt does not powder well. Talc, which is also used for powdering surgical gloves, and two out of five starch powders caused massive adhesions when implanted intraperitoneally under aseptic conditions. Three of the starch powders were satisfactorily absorbed with no foreign-body reactions.

Work is in progress to determine if the sulfate-containing byproduct obtained in producing fermentable sugars from corncobs can be used safely in feeds.

The pharmacological properties of rutin, which the Eastern Regional Laboratory extracted from buckwheat plants, and which promises to be an effective new drug for correcting excessive fragility in capillary blood vessels, are being investigated to explain the many beneficial results obtained with this substance in clinical tests. The reported protective effect of rutin on the hormone epinephrine (adrenalin) was confirmed. This may prove to be important in learning the mechanism of rutin's physiological action.

Ascorbyl palmitate, which the Eastern Regional Laboratory has found to be effective as an antioxidant to retard rancidity when dissolved to a very low concentration in lard, was equal to ascorbic acid (vitamin C) in antiscorbutic effect, as determined with guinea pigs.

The natural alkaloid levo-nicotine, from tobacco, and the synthetic alkaloid myosmine, produced from nicotine by the Eastern Regional Laboratory, were compared with regard to acute toxicity to albino rats.

In order to determine if the removal of pigment glands from cottonseed meal, by the process developed at the Southern Regional Laboratory, has a beneficial effect on the meal as a food material, studies were started on the chronic toxicities of cottonseed meal and the pigment-glands fraction of cottonseed kernels.

Experiments were made in cooperation with the Bureau of Plant Industry, Soils, and Agricultural Engineering on the chronic toxicities of thiourea, thioacetamide and 8-hydroxylquinoline sulfate in order to learn if there is any public health hazard in using these chemicals to prevent stem-end rot in Florida oranges.

## BETTER SOYBEAN MEAL OBTAINED BY MODIFIED ALCOHOL-EXTRACTION PROCESS

The meal obtained in the production of soybean oil is used chiefly in feeds for livestock, but it is recognized as a valuable material for increasing the protein content of foods. This meal would be used more extensively in foods if it were more palatable and of more pleasing appearance. In general, both types of industrial processes now used for separating the oil from soybeans—one being hot pressing and the other extraction with petroleum solvents—yield meals that are not pleasing in color and taste. Since alcohol extraction of oil from soybeans was known to leave a palatable meal, the Northern Regional Research Laboratory started 3 years ago to develop an economically feasible process for extracting soybean oil with alcohol. It now has a continuous alcohol-extraction process almost ready for commercial use. The alcohol is to be recovered for reuse by chilling the solution of oil and alcohol which causes them to separate, thus eliminating the necessity and expense of distillation.

In cooperation with a commercial firm, the extraction of soybean oil with alcohol was carried on in a pilot plant in order to get needed engineering data. A full-sized plant for applying the continuous alcohol-extraction process for soybeans is being designed. Industrial application of the process is expected to lead to lower cost of oil extraction, greater safety in operation, higher quality of oil, and a more palatable soybean meal suitable for making soybean flour or for use in various food products. Of added significance to agriculture is the fact that the solvent, ethyl alcohol, can be made from farm products.

Experiments have shown that bread, meringues, whips, and candies made with soybean flour prepared from the meal of alcohol-extracted soybeans are superior in flavor and color and are equal in nutritive value to similar products made with commercial soybean flour. The protein derived from alcohol-extracted soybean meal is whiter than that derived from meal of soybeans extracted with petroleum solvents and is therefore more suitable for making artificial fibers or in coating papers. Additional studies on possible uses of alcohol-extracted soybean meal and the derived protein are under way.

## EFFORTS MADE TO IMPROVE FLAVOR OF SOYBEAN OIL

The future of the soybean-oil industry depends in large measure on finding means for preventing the rapid development of undesirable flavors in refined soybean oil and food products made from it, such as salad oil, margarine, shortening, and baked goods containing soybean shortening. Since other food oils are less likely to develop bad flavors on standing, they are preferred for use in food products when they are available. During the late war there was large expansion in the production and consumption of soybean oil because of the world shortage of edible oils, but there will probably be considerable contraction in soybean consumption when other edible oils become plentiful, unless the flavor stability of refined soybean oil and its products can be substantially improved.

Research on this problem has been in progress at the Northern Regional Laboratory for the past 2 years. Progress toward its solu-

tion was materially accelerated by information gleaned in Germany by a member of the Laboratory's staff who was loaned to the Technical Industrial Intelligence Committee of the Foreign Economic Administration to investigate the German oilseed processing industry. He learned that the German industry had developed methods which were claimed to produce a soybean oil of practically permanent flavor. In the belief that lecithin, a nitrogen- and phosphorus-containing compound of fatlike character, is responsible for instability of flavor in soybean oil, the German oil refiners removed most of the lecithin before alkali refining by successive washings with water, which forms an emulsion with it. Citric acid was added to the soybean oil during the deodorization process in the belief that it inactivates remaining traces of lecithin.

The German procedure has been tried on a small scale in the laboratory and appears to have distinct merit. Soybean oils treated by this method had definitely higher flavor stability than those refined in the usual way. These results, which were reported at the 1946 annual meetings of the Soybean Oil Processors and the American Oil Chemists' Society, aroused much interest in the soybean-oil industry and have stimulated research and process investigations among others along similar lines.

The ultimate significance of this work to the American farmer and the soybean-processing industry is difficult to gage at this early stage of development. However, it is almost sure to place soybean oil in a more favorable competitive position with respect to other food oils and thus tend to reduce the difference in price between soybean oil and other edible oils.

## GOOD LARD PRESERVATIVES MADE FROM GALLIC ACID

Natural substances or chemical compounds that retard oxidation of fats and oils are useful as lard preservatives because they help to prevent rancidity. The problem is to find antioxidant substances that are soluble in lard and not dangerous to health, and that also improve the baked goods made with lard containing them.

Among the most effective antioxidants known are the esters of gallic acid. Such compounds were prepared by the Eastern Regional Laboratory, without much difficulty, from gallic acid and different kinds of alcohol containing not more than five carbon atoms, but these esters of short-chain alcohols were not sufficiently soluble in fats and were not satisfactory when carried into baked goods.

Esters of gallic acid with longer-chain alcohols having even numbers of carbon atoms—up to and including octadecyl ($C_{18}$) alcohol—were prepared by an indirect and therefore less simple method of synthesis. Laboratory tests indicated that these compounds are sufficiently soluble in fats, have excellent antioxidant properties, and show excellent carry-over of protective action to baked goods. They are belived to be nontoxic, although complete information on this point is not yet available.

Later, the Eastern Regional Laboratory succeeded in developing a new, single-step, direct laboratory method for combining gallic acid with the higher alcohols. This newly discovered method, by means of

which the ester of gallic acid with lauryl ($C_{12}$) alcohol can be prepared in yields above 80 percent, based on quantity of gallic acid used, makes this improved type of gallate antioxidant potentially available at a much lower price than has been possible heretofore.

### ANIMAL FATS SEPARATED INTO COMPONENT GLYCERIDES

Fats are mixtures of fatty acid-glycerol compounds, each glycerol radical being combined with three fatty acid radicals, which may be of one, two, or three kinds in one molecule. The principal acids in fats are the saturated stearic and palmitic acids, whose triglycerides are solid at room temperature, and the unsaturated oleic acid, whose triglyceride is liquid at room temperature. The consistency and other characteristics of fats depend upon the relative proportions of the different kinds of triglycerides present, and 10 different combinations of 3 fatty acid radicals with 1 glycerol radical are possible.

Research at the Eastern Regional Laboratory on the utilization of animal fats resulted in a laboratory procedure for separating lard or tallow into different classes of triglycerides by crystallizing fractions from an acetone or other solution of the fat at different temperatures. It was found possible to obtain fat fractions consisting principally of a single class of triglycerides with regard to radicals of saturated and unsaturated fatty acids, that is, with three saturated; two saturated and one unsaturated; one saturated and two unsaturated; or three unsaturated acid radicals. The results led to the development of a practical method for determining the percentage of triglycerides of saturated fatty acids (including stearate, stearate-palmitates, and palmitate) in fats, such as lard and tallow, whose saturated acids are principally palmitic and stearic. By this method it was also possible to determine rather closely the percentage of each of three other classes of triglycerides—those containing one, two, and three unsaturated (oleic) acid radicals.

It is believed that the data obtained in the laboratory-scale separation of fats into fractions can serve as a background for the development of industrial processes for manufacturing modified fats for special purposes. By using individual fractions or by mixing fractions in different proportions, it should be possible to achieve more desirable properties with regard to consistency, plastic range, shortening power, and creaming quality, and also greater uniformity in the product. The fat fractionation technique is already being used in the laboratory to study the changes that take place during commercial hydrogenation of lard.

### INDUSTRIALLY USEFUL CHEMICALS MADE FROM FATS

The Eastern Regional Research Laboratory developed two methods for converting oleic acid, one of the principal constituents of lard and other fats, into chemical derivatives that are potentially useful in industry. By one method oleic acid, or a similar compound, can be converted into its epoxy (cyclic ether) derivative, which is especially reactive and enables the fat derivative to be used in the preparation of

polymers and additives for lubricants or for the addition of long carbon chains to other compounds. The other method converts oleic acid into dihydroxystearic acid which can be used as an intermediate in the preparation of lubricants, plasticizers, and high-melting synthetic waxes.

In the first method oleic acid is added to peracetic acid (made by mixing 30-percent hydrogen peroxide with acetic anhydride) at a carefully controlled temperature. A high yield of epoxystearic acid is obtained. In the second method oleic acid is added to a mixture of 30-percent hydrogen peroxide and formic acid (or acetic acid containing a little sulfuric acid). The conversion to dihydroxystearic acid is quantitative, requiring only a slight excess of hydrogen peroxide, and the formic or acetic acid can be recovered for reuse. Both methods can be applied not only to oleic acid, but to any fat or fatty acid that contains an isolated double bond.

These methods for converting fats or certain constituents of fats into industrially useful chemicals are suitable for commercial application, and great interest in them has been shown by a number of chemical manufacturers. Their development has served to focus considerably increased attention on fats as possible sources of industrial chemicals.

## FAT DERIVATIVES IMPROVE LUBRICATING OILS

Previous research on the chemical conversion of fats and fat components showed that simple derivatives of certain arylstearic acids, when added in small proportions to lubricating oils, greatly increased the capacity of the oil for rust prevention. This fact was of interest to the Office of Research and Inventions of the Navy Department, and, at its request, the Eastern Regional Research Laboratory prepared numerous compounds of this class for evaluation as oil additives by the Naval Research Laboratory. Many of these compounds also have properties that make them useful for increasing the load-carrying capacity and reducing wear. Although arylstearic acids have molecular weights that are higher than that of solid, crystalline stearic acid, they are viscous oils that do not crystallize. Some of the arylstearic acid derivatives are soluble in both oil and water, and this unusual property makes them useful for certain special purposes. New arylstearic acids and related compounds were prepared, and the method of preparing them was modified so as to require less time.

In general, arylstearic acids are prepared by condensing the fat component oleic acid (an aliphatic or open-chain carbon compound) with benzene or other aromatic (ring-structure) carbon compound in the presence of anhydrous aluminum chloride under controlled conditions. The particular aromatic compound used for combining with the oleic acid influences the yield and properties of the product.

Chemical products of other types prepared from fats were also submitted to the Naval Research Laboratory for evaluation as oil additives.

Considerable attention is being given to the possibility of using fats and oils as raw materials in the chemical synthesis of a lubricant having special desirable properties that are lacking in mineral-oil lubricants.

## PROPER DRYING OF DEHULLED TUNG NUTS NEEDED FOR SATISFACTORY STORAGE AND PROCESSING

Field hullers for tung fruits were introduced during the 1944–45 harvesting season. The general adoption of these portable field hullers during the past season presented problems in proper drying of dehulled nuts at the crushing mills. Since moisture content of tung nuts is a critical factor in the efficient operation of oil expellers, all of the large tung-oil mills are trying to adopt controlled drying of the nuts, whether hulled in the orchards or at the mill. In order to aid them, the Tung Oil Laboratories at Bogalusa, La., and Gainesville, Fla., conducted experiments to determine how all of the factors involved in the drying and subsequent storage of dehulled nuts affect efficiency of expelling and quality of the oil. Data were obtained in cooperation with the Florida Engineering Experiment Station on small lots of tung nuts dried under controlled conditions and pressed in a laboratory expeller. Several lots of about 600 pounds each were dried at controlled temperatures in an experimental tray drier at the Southern Regional Research Laboratory, and data were obtained on these same lots at Bogalusa in mill tests, with a commercial expeller, shortly after drying and also after various periods of storage. It was established that dehulled nuts dried to 10 percent moisture content at air temperatures below 160° F. can be stored for at least 4 months and then processed efficiently to yield high-quality oil. However, nuts dried at temperatures of 180° to 212° F. must be processed promptly, since efficient expelling is not possible after storage. Control samples of high moisture content that were not artificially dried did not process efficiently after storage under ordinary conditions and yielded poor-quality oil.

## EGG POWDER MADE TO KEEP BETTER IN STORAGE

The continuing demand for whole-egg powder, the production of which amounted to over 300,000,000 pounds in the war year 1944, has given increased importance to the need for improving the somewhat unstable quality of this product and preventing its physical and chemical deterioration during storage. Intensive investigations at the Western Regional Research Laboratory have led to a partial understanding of the phases in egg-powder deterioration. the chief of these being (1) formation of aldehyde-amine reaction products, which on spectrophotometric study proved to be correlated with the development of brown color and loss of palatability, and (2) changes in the phospholipids (nitrogen- and phosphorus-containing fatlike components of egg yolk) during storage, which contribute to unpleasant flavors. It is possible that enzymic catalysts, surviving the death of microorganisms that may have been introduced at some point in processing, promote the chemical reactions. By applying the knowledge gained in the fundamental studies, improvements can be effected in the quality of egg powder, and the market for that product can be maintained or expanded.

The increase in storage life is an important factor in assuring the continued peacetime use of egg powder by public and private institutions, by restaurants, and by bakeries. The most tangible accomplishment of the Western Regional Laboratory in this connection is the

development of a method for controlling acidity not only during the drying cycles but also during storage.

The method consists of acidifying the broken-out eggs with hydrochloric acid to a pH of 5.5, before drying, and then neutralizing the acid by mixing with the powder the necessary quantity of sodium bicarbonate. Upon reconstitution of the powder (adding as much water as removed) the reaction between acid and soda forms a small amount of sodium chloride (common salt). The salt thus introduced is not objectionable. By this method the storage life of egg powder was increased fourfold.

Other studies looking toward the prolongation of storage life also yielded good results. For example, in the course of their search for antioxidants, scientists at the Western Regional Laboratory were encouraged to believe that an antioxidant for egg oil, proline, had been found among the amino acids that will prove suitable for extending the storage life of dried eggs.

The studies on dried eggs indicate that the quality of whole-egg powders can be improved and that the storage life can be materially prolonged. By application of the findings, the war-stimulated dried-egg industry, which has continued to hold its own since the war ended, will contribute a valuable service in providing an extended market for eggs. Drying of eggs in spring will help to solve a persistent seasonal surplus problem.

## FOOD-POISONING ORGANISMS SHOULD BE ELIMINATED FROM DRIED EGGS

Data obtained during the recent war from the examination of thousands of samples of spray-dried, whole-egg powder served to emphasize the need for continued research to improve the wholesomeness and keeping quality of dried egg and other egg products. This need has been and is still being further accentuated by the large demands for eggs and egg products in postwar nutrition programs and by the desire of the egg industries to establish a quality basis for greater peacetime consumption.

Many samples of egg powder containing 4 to 6 percent moisture, which had been manufactured in compliance with United States Department of Agriculture and War Food Administration purchase specifications, were found to contain food-poisoning organisms of the *Salmonella* group. Cooperative work with Iowa State College and the Quartermaster Corps of the United States Army brought out the fact that these organisms were readily destroyed in liquid whole egg exposed to pasteurization temperatures, but that the pasteurization of liquid whole egg prior to its dehydration has not been universally required. Although egg powder has not been associated thus far with outbreaks of food poisoning in the United States, the production of even an occasional *Salmonella*-contaminated batch is undesirable. Therefore, in 1946, the Microbiology Research Division extended its *Salmonella* investigations with the ultimate object of determining how *Salmonella* organisms might be eliminated, or at least reduced, in egg products or of devising adequate safeguards against infection. Some of these investigations were undertaken in cooperation with the Quartermaster Corps.

A modification of the Most Probable Numbers Method of Hoskins was found satisfactory for determining the numbers of *Salmonella* organisms in a given egg sample. *Salmonella* organisms remain alive for long periods in contaminated powders stored at room and lower temperatures. They survive when contaminated powder is reconstituted (mixed with water for scrambling) and is held at household refrigerator temperatures. They multiply rapidly when batches of contaminated powder are reconstituted and held at temperatures from 25° to 45° C. (77° to 113° F.), but apparently they die out at 55° C. (131° F.). Cooking by the usual method of scrambling cannot always be depended upon to destroy all the *Salmonella* organisms that may be present in the reconstituted egg mix. Examination of the shell surfaces and meats of eggs from individual hens has not as yet revealed the most probable source of the *Salmonella* organisms that get into egg products.

The Microbiology Research Division's data on dried eggs are being made available to interested Government agencies and are being prepared for publication as rapidly as the studies are completed. As in former years, data obtained through fundamental studies are finding practical application by the egg-processing industries in the selection of raw material, in processing, in laboratory-control programs, in improving plant sanitation, in marketing, and in consumer utilization and handling of egg products. These data should also be useful as a guide in establishing regulatory service and microbiological standards.

### RESEARCH ON FROZEN FOODS LEADS TO BETTER PRODUCTS

The sharp rise in the consumption of frozen foods during recent years has stimulated research on the many problems that arise in connection with preservation of foods by freezing. During the past year the Western Regional Research Laboratory gave special attention to one of the most persistent of these, the tendency of apricots, peaches, and apples to darken during the defrosting stage, and developed a method for use with frozen pie packs that is a distinct improvement over previous methods, which processors did not find entirely satisfactory. The new method comprises (1) blanching with steam for 45 seconds to inactivate skin enzymes, (2) dipping in a sodium bisulfite solution, (3) dipping in a solution of 1-percent ascorbic acid and 2-percent salt, and (4) submerging in a sugar sirup containing ascorbic acid. Its advantages are that the short blanch does not cause leaching, a cooked flavor, or softening and that the salt and ascorbic acid supplement each other in delaying darkening. Fruit undergoing this treatment will not darken until 4 to 6 hours after being defrosted. This provides ample opportunity to cook the defrosted fruit before it has an opportunity to darken. The advantage of the treatment to the pie-baking industry, therefore, is at once obvious.

Jellylike fresh-fruit spreads that retain the full natural flavor, color, and aroma of fresh fruits were made by a cold process from red raspberries, Youngberries, Boysenberries, Loganberries, strawberries, guava apples, red currants, Concord grapes, and Santa Rosa plums. The process involves dissolving powdered pectin in uncooked fruit purees of high soluble-solids content, the solution of the pectin being facilitated by first dispersing it in twice its weight of glycerine. Under

cold processing, the flavor essences that would escape during hot processing are retained. No fruit fragrance permeates the air near cold-processing operations, because the flavor essences are completely incorporated in the products. Although elimination of the heating process saves cost insofar as processing is concerned and also effects a sugar saving of approximately 11 percent, the final conclusion with regard to relative cost of producing the frozen spread must await the results of commercial trials. Regardless of the ultimate findings on this score, the superior flavor of the cold-processed product recommends it instantly to the palate, and widespread consumer acceptance can therefore be expected.

Investigations into the causes for lack of flavor or poor flavor in frozen peas revealed that tardiness in getting the peas from field to processing plant is a major factor in flavor deterioration. In warm weather a delay of 2 hours noticeably reduces flavor quality. The physical and chemical processes responsible for flavor loss can be checked by prompt and thorough cooling of freshly harvested peas.

## DEHYDROFREEZING PROCESS DEVELOPED FOR PRESERVING FOODS

A new process of food preservation that combines most of the advantage of dehydration, namely, reduction in weight and volume, with freezing preservation has attracted much industrial interest. The process, termed dehydrofreezing by the Western Regional Research Laboratory where it was developed, involves carrying the product through the first cycle of dehydration and then freezing. Since the vitamins and flavor are virtually undamaged by this initial dehydration treatment, the product retains the fresh quality and in some instances, notably those of Boysenberries and apricots among the fruit products investigated, it retains the original shape. In consequence of the weight and volume economies, dehydrofreezing effects a saving in packaging materials. The load on refrigeration systems is also materially reduced. Reconstitution of dehydrofrozen foods is easier than that of dehydrated foods because of the greater moisture content of the former. The implications for the fruit and vegetable industries are lowered transportation, storage, packaging, and refrigeration costs. The possibility of utilizing high-altitude freezing in lieu of processing by means of a refrigeration system, for shipments of perishables by air, suggests another avenue of usefulness for dehydrofreezing and a further economy.

A means for improving the technique of designing and controlling dehydrators has been developed at the Western Regional Laboratory through the application to dehydration practices of modern physical theories for the phenomenon of diffusion of water in solids.

## BUREAU'S PEA-CLEANING PROCESS USED BY CANNERS IN NORTHWEST

The novel froth-flotation process for removing nightshade berries and seeds of other weeds from mechanically harvested and shelled peas, which was developed by the cooperative Fruit and Vegetable Byproducts Laboratory at Pullman, Wash., and described in the annual report for 1944, has been used by pea canners in the North-

west, where contamination with nightshade berries is troublesome. During the 1946 season the cleaning process was in large-scale commercial use at four canneries that had installed "in line" machines capable of cleaning from 2 to 4 tons of shelled peas per hour. General adoption of the process in the 1947 season is expected.

The removal of nightshade berries by hand, while the shelled peas pass by on inspection belts, requires so much labor as to be impractical at times. For this reason, heavily contaminated lots of peas have often been rejected, or portions of fields badly infested with nightshade weeds have not been harvested. Definite data on the amount of labor saved by the use of the pea-cleaning machines will not be available until complete reports are received from the commercial operations mentioned, but it is believed that 50 percent is a conservative estimate. Since quick handling is an important factor in maintaining the quality of canning peas, and mechanical cleaning is much more rapid than hand cleaning, the pea-cleaning process confers another benefit on the pea-canning industry.

An automatic regulator for use with the previously designed pea-cleaning machine was recently developed by the Fruit and Vegetable Byproducts Laboratory. This device controls the surface tension of the emulsion used in making the flotation separation of contaminants and thus permits more exact regulation than could be accomplished by hand. An application for a public-service patent to cover this regulator has been filed.

## BUREAU AIDS WESTERN FRUIT PROCESSORS IN SOLUTION OF TECHNICAL PROBLEMS

In cooperation with processors of California and Arizona grapefruit, the Laboratory of Fruit and Vegetable Chemistry at Los Angeles has continued its work on the modification of canned grapefruit juice to attain uniformly acceptable quality throughout the packing season. The so-called desert grapefruit grown in Arizona and southern California has inherent characteristics which affect the processed juice more or less unfavorably, depending on the time of harvesting. The juice processed in certain portions of the season is either too tart or too bland for most persons, whereas that processed at other times is very acceptable. It is obvious that consumers will not respond well to any brand of canned juice that is sometimes excellent in flavor and sometimes unsatisfactory. In order to compete successfully with canned grapefruit juice processed in other growing areas, it is necessary for the rapidly growing grapefruit-processing industry in the Arizona-California area to develop a uniformly good canned juice.

Attention has been given to various phases of the problem, including determination of the acid-sugar ratio of an ideal juice processed from desert grapefruit, the amount of neutralizing agent needed to suppress excessive tartness in juices of various acid contents, and the amount of sugar needed to attain the sweetness of the ideal juice when added to juices lacking in sweetness. Experiments have also been made to determine the keeping quality of the modified grapefruit juice and the causes that contribute to the development of unpleasant flavors. Although work on this project has not been completed, interested grapefruit processors appreciate the progress that has been made toward stabilizing the demand for canned desert grapefruit juice.

Incidental to work on the major problem of producing a uniform juice, analytical methods of value for control work in grapefruit processing were developed. These include a method for determining the bitter glycoside, naringin, in grapefruit juice and a method for checking the effectiveness of the de-aeration step by determining dissolved oxygen in the juice.

In cooperation with California date growers, the Laboratory of Fruit and Vegetable Chemistry developed a method for cleaning dates that is less costly, more effective, and more sanitary than the usual method of rolling the unwashed dates down an incline covered with Turkish toweling. The new method consists of passing the dates under a spray of clean warm water and then under a blast of warm air. Exposure of the cleaned dates for a short time to the rays from an infrared lamp is recommended, since this treatment temporarily softens the natural waxy coating on the surface of the dates and gives them a glossy appearance that appeals to consumers.

## PROGRESS MADE IN ISOLATING CHEMICAL COMPONENTS OF CITRUS FRUITS

The Agricultural Chemical Research Division has investigated the components of citrus fruits, particularly the lipid or nonvolatile-oil fraction, in order to isolate and study compounds suspected of playing an important role in deterioration of flavor of canned juices in storage. A method was developed in the Citrus Products Laboratory at Winter Haven, Fla., for adsorbing this fraction on processed diatomaceous earth, and it was established that the lipid materials are thus obtained quantitatively much more efficiently than by extraction with solvents. Large batches of oranges were cut into pieces, pulped, and filtered on diatomaceous earth at Winter Haven, and similar material was prepared from grapefruit in the Fruit and Vegetable Products Laboratory at Weslaco, Tex. The filter cakes were sent under refrigeration and with a preservative added to New Orleans for chemical study.

At the New Orleans Laboratory the filter cakes wer extracted with ether, and the extracts were fractionated with various solvents. Thus far, a crystalline phytosterol, a fatty acid, and a phosphatide have been isolated from grapefruit and partly analyzed. Determination of the structure of these compounds is expected to indicate their possible role in the development of unpleasant flavors. Similar substances have been separated from orange-pulp extracts and are being compared with those from grapefruit.

A thorough study was made of the nature of the deposits located in or between the vesicles or juice sacs of oranges and grapefruit. These deposits have been reported to be oil, but the fruit examined thus far has not revealed discrete oil globules. Microchemical tests on numerous samples to determine their reaction with various dyes showed that the deposits stained by fat-soluble dyes consist of waxy cork tissue. Isolation of phellonic acid, a constituent of the waxy substance suberin, from the ether extracts of the filter cakes containing the lipids of orange and grapefruit pulps lends support to the conclusion that the deposits in question are not fatty oils. Much fundamental knowledge of this kind is needed as a basis for sound, practical work on the problem of flavor deterioration in canned citrus juices.

## CHEAPER PECTIN IN PROSPECT FOR FOOD USES

As the result of studies on modified (low-methoxyl) pectin and the development of new products containing it, this material may soon be produced commercially from fruit wastes at a cost appreciably less than that of producing pectin by the alcohol method, which is generally used. The Western Regional Research Laboratory's method, which is based on a continuous countercurrent extraction that isolates the low-methoxyl pectin by acid, is under pilot-plant test at an industrial plant in southern California where citrus wastes are available in quantity. The method can also be applied to other waste fruits, and an economic analysis to determine the feasibility of using apple thinnings for pectin production is under way. A large tonnage of immature apples is removed from the trees annually by commercial growers, but the problem is to concentrate the supply in order to assure economic processing.

Other studies on pectin have yielded fundamental technical and scientific information of potential usefulness. The results ranged from the development of a rigidometer for determining the jelly grade of pectin to determinations of the film and fiber qualities of pectinic acids. In the latter investigations fibers and films were obtained with tensile strengths in the range of 60,000 pounds and 17,000 pounds per square inch, respectively. In the fiber the relative position of the atoms provides excellent chances for arrangement of the molecules in parallel lines; the fiber is therefore strong and fairly elastic. Although the film prepared from pectinic acid has low shear resistance, it has flexibility as well as other qualities useful commercially. It shows promise as a casing for sausages where its low shear resistance would be advantageous. Perhaps of prime importance in this use would be the light, transparent color of the film, since this color would enhance the appearance of the sausage product and add to its consumer appeal.

## FLAVOR RECOVERED FROM APPLES AND ORANGES

Last year's report told about a process for recovering the volatile flavor constituents from fruit juices, especially apple juice. In the past year nine companies (six in the United States and three in Canada), set up equipment for the process, but could make only small amounts of apple essence because of the severe apple shortage. There were prospects of these and other companies making apple essence from the 1946 crop.

The latest work along this line at the Eastern Regional Research Laboratory was confined largely to a comparison of the following apple varieties as sources of essence: McIntosh, Jonathan, Stayman Winesap, Grimes Golden, Baldwin, Red Delicious, Golden Delicious, Northern Spy, and Rhode Island Greening. Essence from each variety had its own characteristic aroma which closely followed the individual character of the apples from which it was produced. The various essences were compared by using them in: (1) Full-flavored apple concentrate which was diluted to a beverage; (2) gum-type apple candy; and (3) apple jelly.

The best essences as regards both intensity and pleasantness of flavor were from McIntosh and Delicious (Red and Golden) apples.

Stayman, Jonathan, and Baldwin essences were rated as good, Grimes Golden and Northern Spy as only fair, and Rhode Island Greening as poor. Since in most apple regions blends of varieties have to be used, for practical reasons, the above evaluations can serve only as a general guide; but where some choice of varieties can be exercised, these ratings should prove useful.

In order to determine the feasibility of recovering the volatile flavor constituents of orange juice by the same method as developed for apple juice, the flavor recovery equipment was shipped to this bureau's citrus products laboratory at Winter Haven, Fla., where fresh orange juice was available in quantity. Vaporization of 10 to 15 percent of the orange juice in a single-pass evaporator removed all of the detectable volatile flavors. When condensed, these flavors consisted of an oil phase from the rind and a water phase from the juice. By evaporation at atmospheric pressure the flavor in the water phase could be concentrated to about a hundredfold without incurring any significant loss or change in its character.

The orange juice essence (concentrated volatile flavor in the water phase) was somewhat similar in its ethereal character to apple essence, but at the same relative concentration (referred to fresh juice) it was much milder as a flavoring material. When mixed in normal proportions with a drink reconstituted from orange concentrate, it tended to mask the cooked and other off-flavors which had developed during processing and storage.

## NEW AGRICULTURAL PRODUCTS USED IN CANDY

The Agricultural Chemical Research Division has cooperated with the National Confectioners' Association in a study of the possibilities of using a wider variety of agricultural products in confectionery, particularly such as will balance the carbohydrate by increasing protein, fat, and vitamin contents of candy. Steady progress has been made, and the protein contents of certain types of candy which usually contain less than 1 percent have been increased to as much as 5 to 6 percent without impairing flavor or quality. A total of 8 percent protein is considered to be adequate for a balanced food, if the protein is of high nutritional value. New types of food yeast are most promising as sources of vitamin B complex and niacin, as well as good-quality protein, for use in certain kinds of candy. For high-grade candies it is necessary to use refined proteins, rather than soybean or peanut flour, to avoid objectionable texture and flavor. In preliminary trials a refined peanut preparation, containing more than 90-percent protein, was used with some success. Similar isolated protein products from soybeans, developed at the Northern Regional Research Laboratory and by soybean processors, have been incorporated in nougats, vanilla chews, and cast creams in amounts up to 3 to 4 percent with satisfactory results.

Other edible products, developed by the Bureau's laboratories, which do not contribute directly toward the nutritional balance of candy have been used successfully in developing new types of pieces. For example, modified pectin, produced at the Western Regional Research Laboratory by alkali demethylation of pectin, has been used by the Agricultural Chemical Research Division to make inter-

esting new jellies and a radically new cream-type center. Unlike ordinary pectin, which requires a high sucrose concentration for gelling, this low-methyl ester pectin gels with milk solids, dextrose sirup, or fruit pulps when calcium is present, even when no sucrose is included in the formula. Excellent jellies have been made in which more than half of the sucrose ordinarily used was replaced by an equal weight of corn-sirup solids. The new cream-type center is made with relatively little sucrose, a creamy butterscotch-flavored gel being produced by adding a little modified pectin to a mixture of sucrose, powdered milk, and corn-sirup. The total carbohydrate content of this cream center is about three-fourths that of ordinary fondant centers and the sucrose content is less than one-fourth. When the molded center is dipped in chocolate it makes an excellent candy, although it contains half again as much water as there is in chocolate creams made with ordinary cream fondant. Apple-flavored candies were developed at the Eastern Regional Research Laboratory by using apple sirups and flavoring essences produced by the process developed there for recovery of true apple essence. Apple-jelly pieces of outstanding quality were produced, and very superior apply flavors were imparted to other types of candy.

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